SOUTHERN CALIFORNIA AIR QUALITY STUDY - FALL STUDY

Contract No. ARB A732-089

FINAL REPORT

July 1988

Prepared by

B.R. Appel, Y. Tokiwa, and V. Povard

Air and Industrial Hygiene Laboratory
California Department of Health Services
2151 Berkeley Way
Berkeley, California 94704-9980

Submitted by

Submitted to: John Holmes, Ph.D., Chief
Research Division
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

ABSTRACT

A field study was performed as part of the Air Resources Board-sponsored Southern California Air Quality Study (SCAQS). Sampling was done at Long Beach Community College for six, 24-hr periods from within the interval November 11 to December 12, 1987. Sampling focussed on the measurement of nitrogen oxides and ammonia. Nitrous and nitric acid, as well as hydrochloric acid, were sampled with carbonate-glycerol-coated annular denuders. Nitrogen dioxide was measured with a chemiluminescent NO_x analyzer which sampled half the time through carbonate-glycerol coated open tubes intended to remove the interferents, HONO and HNO_3. Ammonia was sampled with citric acid-glycerine-coated annular denuders, and analyzed on-site to minimize error. The sampler design ensured that NH_3 loss ahead of the collection surface was minimized. Other pollutants measured, to assist in data analysis, included NO and O_3, relative humidity and temperature.

Nitrogen dioxide measured with the denuded chemiluminescent analyzer averaged about 13% lower than without the denuder. Nitrogen dioxide, itself, was shown to have nearly quantitative transmission efficiency through the denuder. The concentration of the interferent removed by the denuder showed positive correlation with the sum of HONO and HNO_3. Nitrous acid concentrations exhibited diurnal maxima between midnight and 0600 hours, with 6-hr mean concentrations up to 14 ppb. However, unexpectedly high daytime HONO concentrations of 3 or 4 ppb were often observed, suggesting that artifactual HONO (e.g. that possibly formed within the inlet) may contribute to the measured values. Nitric acid showed diurnal maxima during the 1000 - 1400 hours sampling period, with levels up to 16 $\mu g/m^3$ (6 ppb). The concentration of HCl also exhibited a consistent diurnal maximum between 1000 and 1400 hours, with concentrations up to 15 ppb. Thus, HCl may be a relatively important source of acidification, by wet and dry deposition, near the western edge of the South Coast Air Basin.

Ammonia concentrations exhibited maxima during night or morning hours, with four or six hour average concentrations up to 15 ppb. Comparison of the ammonia results with those from the SCAQS sampler suggests a substantial degree of NH_3 loss within the latter sampler.

TABLE OF CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

I. SUMMARY AND CONCLUSIONS

A field study was performed as part of the Air Resources Board-sponsored Southern California Air Quality Study (SCAQS). It is referred to as the Fall SCAQS to distinguish it from the summertime SCAQS, completed during the period July-September 1987. Sampling was done in parallel with other investigators at Long Beach Community College for six, 24-hr periods from within the interval November 11 to December 12, 1987. Our sampling focussed on the measurement of nitrogen oxides and ammonia. Nitrous and nitric acid, as well as hydrochloric acid, were sampled with carbonate-glycerol-coated annular denuders, followed by conventional laboratory analysis. Samples were refrigerated immediately, and analyses completed within one week of collection to minimize degradation of HONO samples collected as NO_2^-. The Teflon-coated glass cyclone used as the sampler inlet was previously shown to minimize collection of nitric acid. Prior results also suggested the absence of substantial HONO formation on the walls of this cyclone. Nitrogen dioxide was measured with a chemiluminescent NO_x analyzer which sampled half the time through carbonate-glycerol coated open tubes intended to remove the interferents, HONO and HNO_3. The interferents removed, measured by difference, were termed NO_y. Using a single channel NO_x analyzer, the difference technique was subject to substantial error during periods of rapidly changing nitrogen oxide concentrations.

Ammonia was sampled with citric acid-glycerine-coated annular denuders, and analyzed on-site to minimize error. The relatively high sampling rate (17 Lpm) of the annular denuders provided a sample size sufficient to insure good analytical precision. The sampler design ensured that NH_3 loss ahead of the collection surface was minimized. Other pollutants measured, to assist in data analysis, included NO and O_3, relative humidity and temperature.

Nitrous acid concentrations exhibited diurnal maxima between midnight and 0600 hours, with 6-hr mean concentrations up to 14 ppb. Nighttime maxima are consistent with the photochemical instability of HONO. Short term, nighttime maxima up to 10 ppb were previously observed by UC (Riverside) personnel at El Camino College (Torrance) using dual optical absorption spectrometry (24), similar to results in the present work. However, in the present study unexpectedly high daytime HONO concentrations of 3 or 4 ppb were often observed, suggesting that artifactual HONO (e.g. that possibly formed within the inlet) may contribute to the measured values. Reduced solar UV intensity during the Fall period should enhance daytime steady-state concentrations of HONO relative to concentrations measured during the more extensively studied summer period. Nevertheless, these concentrations are much higher than expected. Analytical error appears unlikely to have caused elevated HONO results. The accuracy of these HONO measurements cannot be properly assessed until spectroscopically measured HONO results become available, a constraint which prevents such comparisons within the present report.

Nitric acid showed diurnal maxima during the 1000 - 1400 hours sampling period, with levels up to 16 $\mu g/m^3$ (6 ppb). The O_3 maxima generally followed those for HNO_3, which contrasts with summertime behavior in Claremont and Riverside. As with HONO, parallel measurements with other methods are not yet available.

The concentration of HCl also exhibited a consistent diurnal maximum between 1000 and 1400 hours, with concentrations up to 15 ppb. Such levels are much higher than found earlier at Claremont and Riverside. Thus, HCl may be a relatively important source of acidification, by wet and dry deposition, near the western edge of the South Coast Air Basin.

Nitrogen dioxide measured with the denuded chemiluminescent analyzer averaged about 13% lower than without the denuder. Nitrogen dioxide, itself, was shown to have nearly quantitative transmission efficiency through the denuder. The concentration of NO_y (i.e. the interferent removed by the denuder) showed positive correlation (r=0.67) with the sum of HONO and HNO_3, with a molar ratio of mean NO_y to mean (HONO + HNO_3) of 0.71.

Ammonia concentrations exhibited maxima during night or morning hours, with four or six hour average concentrations up to 15 ppb. The observed levels are quite high, relative to summertime NH_3 levels measured at Torrance (6) and Lennox (21). Comparison of the ammonia results with those from the SCAQS sampler operated at Long Beach by Environmental Monitoring & Services, Inc. (EMSI) suggests a substantial degree of NH_3 loss within the latter sampler. Although a split sample comparison showed EMSI's NH_4^+ analyses to average 40% higher than those by AIHL's specific ion electrode method, atmospheric concentrations with the SCAQS sampler averaged about 30% lower.

The principal conclusions from this work are:

1. The annular denuder method provides a relatively simple, low-cost method to measure atmospheric HONO.

2. Apparent HONO concentration maxima can exceed those for nitric acid at a site near the western edge of the South Coast Air Basin. The accuracy of these HONO measurements cannot be assessed as yet.

3. The routine measurement of atmospheric NO_2 employed by the ARB is subject to error. In the present study, the error averaged 13%, but may be much more severe at sites with elevated levels of HNO_3 and PAN (e.g. Claremont and Pomona). A denuder provides a simple technique to decrease the error of such measurements.

4. Hydrochloric acid may be a relatively important source of acidification by wet and dry deposition at sites near the western edge of the South Coast Air Basin. Airborne concentrations of this acid should be assessed, based on existing data, to evaluate both seasonal and spatial variations in its concentration.

5. Additional evaluations of NH_3 loss within the SCAQS sampler should be made and the units modified as necessary.

II. INTRODUCTION

A. Objectives

1. To measure atmospheric NO_2, with and without correction for interferences, using the chemiluminescent NO_x analyzer technique.

2. To measure atmospheric HNO_3, HONO, HCl and NH_3 with annular denuder techniques.

B. Nitrogen Dioxide Measurement by the Chemiluminescence Technique

The continuous chemiluminescence technique for nitrogen oxides was first reported by Fontijn et al. (1). Nitrogen dioxide is measured by subtracting NO concentrations from those for total nitrogen oxides (NO_x) following conversion of the latter to NO over a catalyst at high temperature:

$$NO_2 = NO_x - NO \qquad (1)$$

The measurement of NO_2 by this approach is subject to positive interference, since any species convertible to NO over the catalyst (usually a molybdenum catalyst at about 300°C) would be indistinguishable from NO_2. A study carried out at the Statewide Air Pollution Research Center, U.C. at Riverside (SAPRC) (2) concluded that PAN was a 100% positive interferent, while both HNO_3 and an alkyl nitrate provided partial interference. More recent work suggests that HONO would also be indistinguishable from NO_2 with a chemiluminescent NO_x analyzer (3). Accordingly, we may write:

$$Obs. \ NO_2 = NO_2 + PAN + HONO + fHNO_3 + fRNO_3 + other \qquad (2)$$

In equation (2), the "f's" indicate contributions from a fraction of the species indicated. "Other" pollutants may include N_2O_5 and alkyl nitrites.

During the ARB-sponsored Nitrogen Species Methods Comparison Study (NSMCS), one participant sought to increase the accuracy of chemiluminescent analyzer (CA) NO_2 measurements by addition of a Nylon filter to the sampling line. Such filters are well known to provide efficient retention of HNO_3 at dosages far in excess of those in ambient air sampling (4). The results of the addition of Nylon filters are illustrated in Figure 1, which plots the ratio of NO_2 results by three analyzers to those by differential optical absorption spectroscopy (DOAS)(13). The tunable diode laser method (TDLAS) (5) showed excellent agreement with the DOAS. Addition of the Nylon filter to the CA operated by Atmospheric Environmental Services, Canada (AES) for the 12-hour sampling periods, coded 56 through 86, eliminated positive deviations, previously up to 40%. These findings suggested that one or more of the species exhibiting diurnal maxima during daylight hours (i.e. PAN, HNO_3, RNO_3) were significant as interferents, with HNO_3 strongly implicated.

-3-
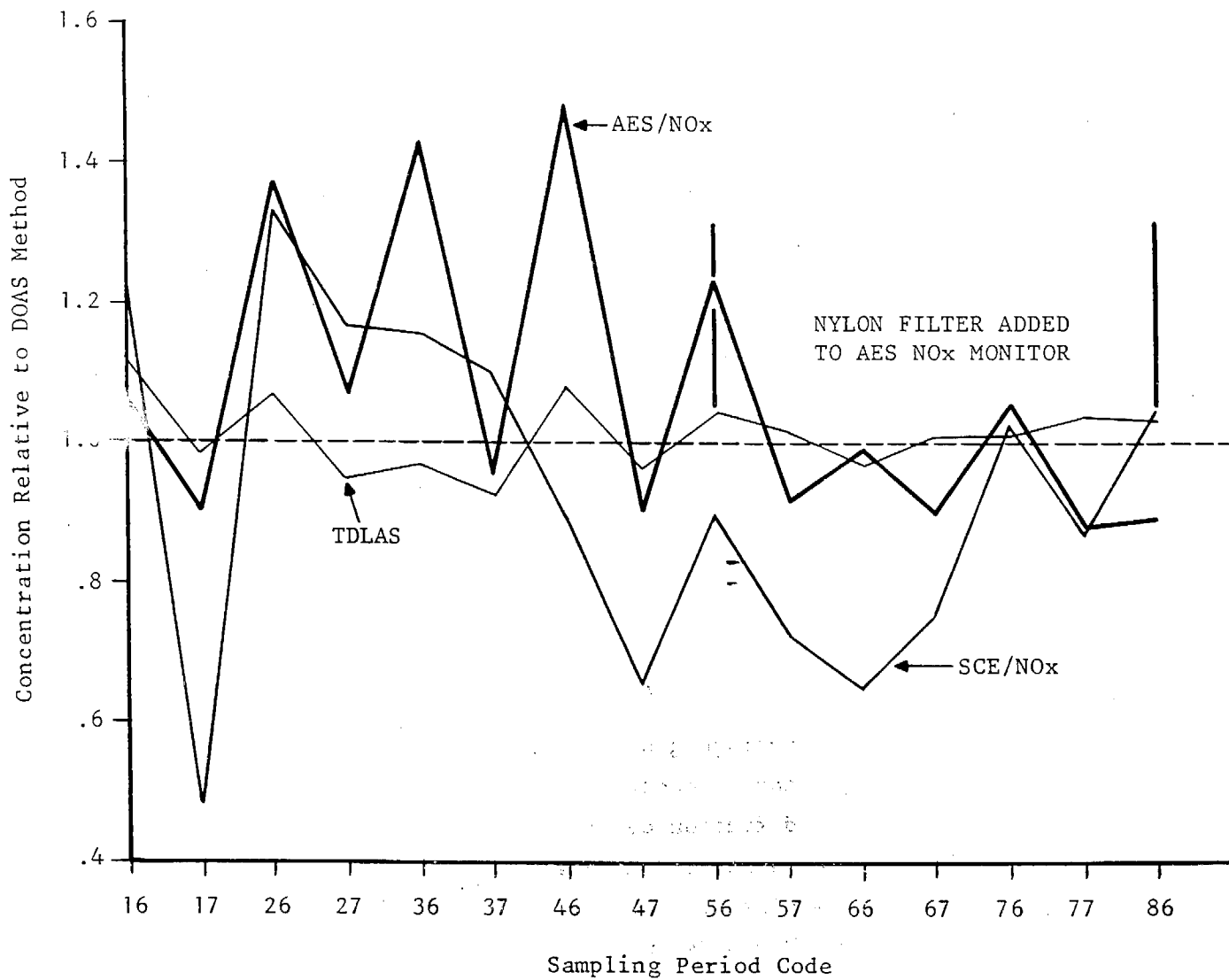
Figure 1. NITROGEN DIOXIDE MEASUREMENTS AT THE NSMCS
WITH AND WITHOUT A NYLON PREFILTER.

The efficiency of HONO removal at 20 Lpm by 47 mm Nylon filters (Gelman Nylasorb) was evaluated in an earlier study (6). At this flow rate, the efficiency for HONO retention was too low to be measured, but, because of interferents, could have been as high as 50%. Prior work with a tube packed with Nylon wool (7) showed relatively high efficiency for HONO retention. Accordingly, at sufficiently low flow rates with Nylon filters (e.g. <1 Lpm with the chemiluminescence analyzer), more efficient removal is probable. High HONO removal efficiency was recently observed for Nylasorb filters ahead of a CA (3).

C. Nitrous Acid, Nitric Acid, and Fine Particulate Nitrate Measurements with an Annular Denuder System

Denuder tubes have been employed for a number of years for collection and measurement of pollutant gases. With single, open bore tubes, relatively low flow rates are required which, in turn, lead to relatively long sampling times for pollutants at ambient concentrations. For example, we have employed 12-hr sampling of NH_3 with a denuder tube at 1.5 Lpm (8). Alternatively, parallel denuder tubes can be used, but the necessity of preparing and recovering chemical species from numerous tubes makes such strategies impractical.

In 1983, a more efficient design was introduced in which the annulus between two concentric cylinders was coated and used as the collection medium (9). The efficiency of such annular denuders can be calculated with the equations:

$$\frac{c}{c_o} = 0.819 \exp(-14.6272 \Delta_a)$$

$$\Delta_a = \frac{DL}{\nu Re \delta}$$

where: c = average gas concentration leaving the denuder

c_o = gas concentration entering the denuder

D = diffusion coefficient of the gas (cm^2/sec)

L = length of the coated annulus (cm)

ν = kinematic viscosity of air (0.152 cm^2/sec at 20°C)

Re = Reynolds number

δ = equivalent diameter of annulus (cm)

The equivalent diameter, $\delta = d_2 - d_1$ where d_1 and d_2 are the inside and outside diameters of the annulus, respectively.

The annular denuder method (ADM) has been evaluated for use in measuring atmospheric SO_2 as well as the acidic gases HNO_3, HONO, HCl and the alkaline species, NH_3 (10). For SO_2, for example, with $D=0.136$ cm/sec^2, efficiencies greater than 97% were observed at 20 Lpm (9).

Annular denuders coated with Na_2CO_3 or Na_2CO_3-glycerine have been used for the collection and subsequent extraction and analysis of atmospheric HNO_3 and HONO (10-12). Measurement of HONO on such denuders appears to be subject to error from atmospheric NO_2 by two different mechanisms. The first results from the partial retention of NO_2 on the collection medium, and the second, from the formation of HONO on the sampler inlet, and, perhaps, on other surfaces within the sampler. Both would result in a species analyzed as NO_2^-, indistinguishable from that due to atmospheric HONO. As discussed below, NO_2^- may also result from chemical reactions involving organic nitrogen oxides.

We previously found that <0.2% of the NO_2 (when freed of HNO_3 and HONO) is retained on a CO_3^--glycerine coated annular denuder at a flow rate of 17 Lpm (6). Assuming 4-hour sampling of 0.1 ppm NO_2 (185 $\mu g/m^3$) at this flowrate; however, <0.2% retention corresponds to up to 1.5 $\mu g/m^3$, a significant error in measuring atmospheric HONO. For this reason, atmospheric HONO concentrations are measured by sampling with two annular denuders in series. The NO_2^- recovered from the upstream denuder represents, at a minimum, the sum of HONO and the small percent NO_2 retained, whereas the NO_2^- recovered from the downstream denuder has been taken to be only that from NO_2 retention, permitting correction by subtraction.

However, prior studies have found NO_2^- values on the downstream denuder to be much higher than expected from our results on NO_2 collection. Based on two years of atmospheric sampling in Calgary (Alberta, Canada), Peake found an average NO_2^- concentration on upstream and downstream annular denuders to be 0.79 ± 0.07 and 0.08 ± 0.02 $\mu g/m^3$, respectively. Thus about a 10% correction was applied (25). Sjodin and Ferm reported that hydrolysis of PAN in alkaline solution to form NO_2^- may be a source of interference (11). Their results suggested that the interference did not exceed 10% of the PAN concentration. For nine sampling periods in January, in Gothenburg, Sweden, NO_2^- on the downstream hollow glass tube denuder averaged 27% of NO_2^- collected on the upstream denuder. The coating in this case was Na_2CO_3 (i.e. no glycerine was used). These authors believed that NO_2^- formation within the sampler was important. Thus, although HONO sampling with carbonate-coated denuders is simple, the interpretation of the resulting NO_2^- data is problematic and required evaluations against more accurate procedures.

Figure 2, provided by D. Lawson, ARB, compares HONO measurements obtained with four devices at the NSMCS. These included two ADM systems, as well as the DOAS, and a metal oxide-coated hollow tube procedure, identified here as HT, as employed by R. Braman (14). DOAS was taken to be the reference method, showing that all of the alternative techniques were subject to a positive bias. Figure 3 is a scatter diagram of the difference in apparent HONO with the two ADM units against NO_2 concentrations. The higher ADM results were obtained by Allegrini et al. (Consiglio Nazionale delle Ricerche, Rome), and the lower set, by E. Peake (University of Calgary, Canada). The former employed a polytetrafluoroethylene (PTFE) cyclone and manifold ahead of the collection medium, whereas Peake's sampler used only a PTFE cyclone. Thus greater surface

Figure 2.

HONO Measurements at the NSMCS
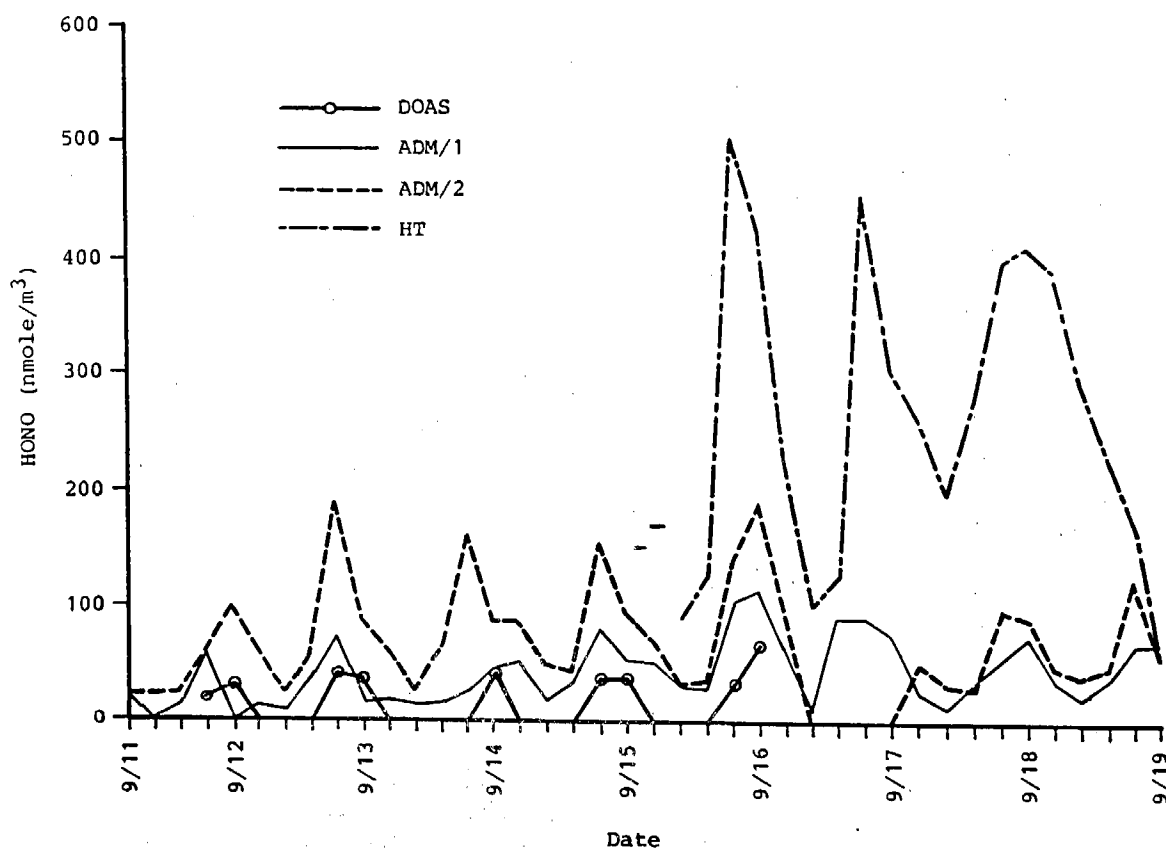
Figure 3

Difference in HONO Measured at the NSMCS
by Two ADM Samplers Against NO_2 Concentrations

$Y=-12.9 + 0.0254X$
$r=0.70$

NO2 (NMOLES/M3)
(Thousands)

DIFFERENCE IN HONO (NMOLES/M3)
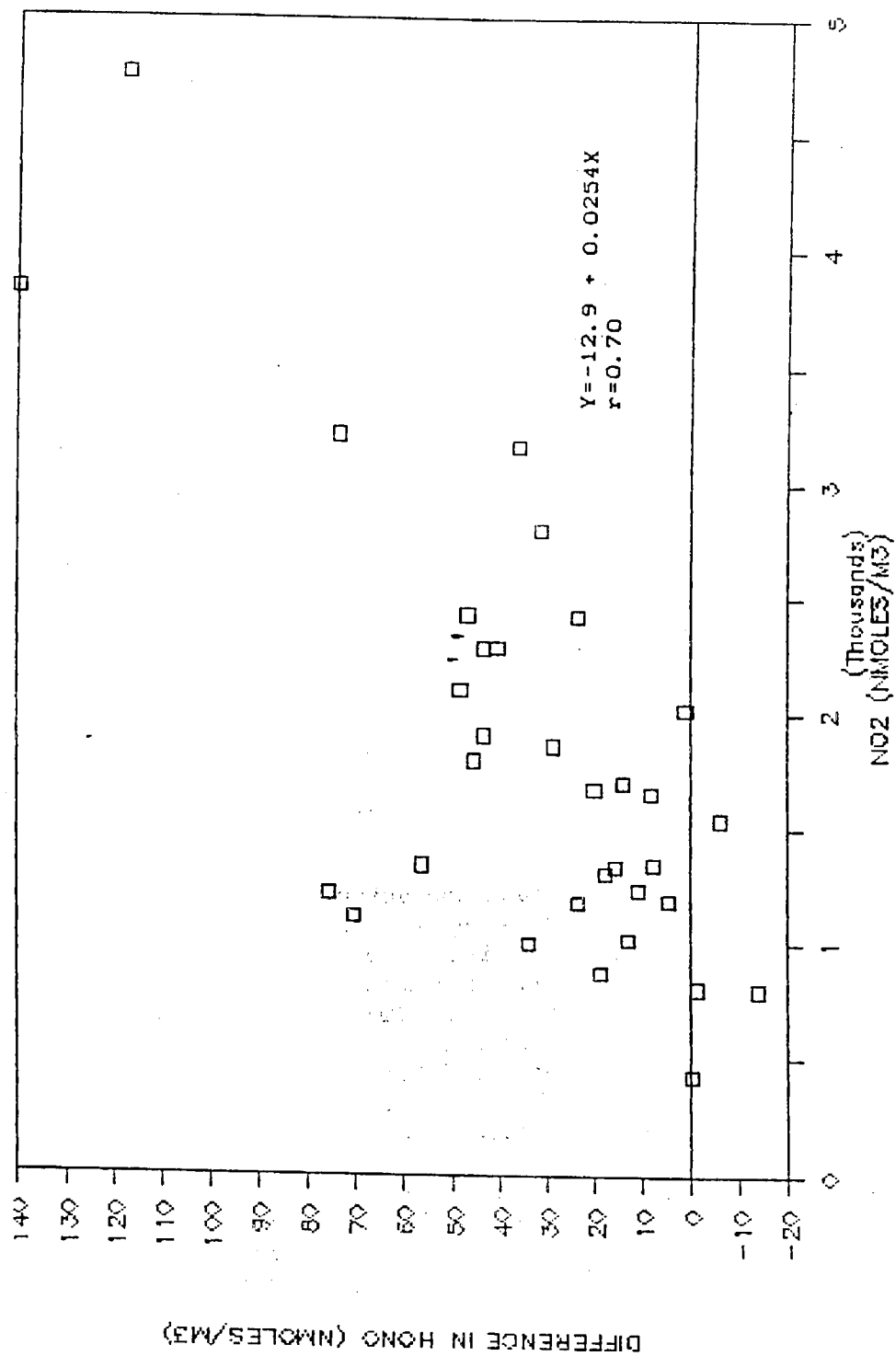
area was available ahead of the collector in Allegrini's system. These observations are consistent with the formation of artifact HONO by the reaction (15,16):

$$2NO_2 + H_2O \xrightarrow{Wall} HONO + HNO_3 \qquad (3)$$
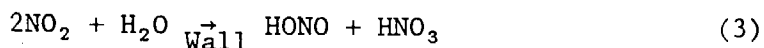
Omission of a cyclone may be a workable strategy for sampling of atmospheric HONO, although the accuracy of such measurements remains to be established. However, HNO_3 measurements without a device excluding coarse particulate nitrate are subject to positive errors (17). This follows because coarse particulate NO_3^-, collected on the denuder by impaction or other mechanism, would be indistinguishable from HNO_3. A Nylon filter placed downstream of such an annular denuder provides a measure of particulate NO_3^-. Partial loss of coarse nitrate particles in the annular denuder would cause a corresponding negative error in measuring the total particulate nitrate. A cyclone or other device to remove coarse nitrate permits the accurate measurement of fine particulate nitrate. A similar argument applies to the measurement of atmospheric HCl.

D.   Ammonia Measurement

Our previous studies (8) have evaluated both a filter pack and an open tube denuder technique for collection of atmospheric ammonia, with subsequent laboratory analyses using a specific ion electrode. The denuder approach, using single, open bore tubes at 1.5 Lpm, showed good agreement, on average, with results by the FTIR technique. However, the low sampling rate restricted the collection time to relatively long periods (e.g. 12 hours). The filter pack technique gave results which were too high by about 50%. The annular denuder method (ADM), described above, is well suited to permit higher sampling rates (e.g. 17 Lpm) and, therefore, sampling periods of 4 to 7 hours with comparatively good analytical precision (18).

At the Long Beach Community College sampling site, a SCAQS sampler (22) was operated by AeroVironment, Inc. personnel for various pollutants, including ammonia. Because of the low atmospheric concentrations of ammonia expected at this site and the low NH_3 sampling rate of the SCAQS sampler (4 Lpm), it was anticipated that a substantial fraction of the resulting ammonia data would be at or below the limit of detection. Furthermore, the substantial inlet surface ahead of the collection medium in this sampler made NH_3 losses of possible significance.

The principal limitation of the ADM for such NH_3 measurements is the comparative instability of NH_4^+ in the aqueous extracts of the denuder coatings. Such instability is believed to be associated with bacterial action and has in the past been dealt with by addition of bactericides or by rapid analysis of samples following sampling. Since the annular denuders are relatively expensive, the tubes are extracted and recoated at the sampling site, leading to possibly substantial delays before NH_4^+ analysis.

Oxalic acid or oxalic acid-glycerine has been the most frequently employed collection medium, either impregnated on filters or as a denuder coating. Recent studies (10) have employed citric acid, advantageous for its lower toxicity. Initial indications are that its collection efficiency is similar to that for oxalic acid.

III. EXPERIMENTAL

A. Scheme for Atmospheric Sampling and Analysis

Table 1 describes the samplers employed, sampling conditions and species measured. The schedule followed for the two annular denuders was about the same as that used for the SCAQS sampler:

Sampling Period	Time (Hours PST)
1	0000-0550
2	0600-0950
3	1000-1350
4	1350-1750
5	1800-2350

Table 2 summarizes the resulting samples analyzed. All aqueous extracts of denuder samples were refrigerated until ready for analysis. Ammonia analyses were done by the specific ion electrode method at the sampling site within 18 hours of sample collection. Extracts from the $CO_3^=$-glycerol-coated denuders were analyzed for NO_2^-, NO_3^- and Cl^- by ion chromatography after return to the laboratory. IC analyses were completed within one week of sample collection.

B. Measurement of NO_2

The measurement strategy using a chemiluminescent NO_x analyzer (CA) and denuders is shown schematically in Figure 4. *For removal of the interferents HONO and HNO_3, the sample was drawn through two, 30 cm glass tubes coated (after etching with HF) with a solution containing 1%w Na_2CO_3 and 1%w glycerol.* A 3-way Teflon solenoid valve permitted sampling of ambient air with or without passage through the denuder. The solenoid was operated by a Chrontrol programmable timer, and sampled for 15 minutes with and then without the denuder. This provided, every hour, two 15-min periods with, and two 15-min periods without the denuder. The average of the two periods with the denuder was taken as a measure of the one-hour average concentration of NO_2. The average concentration from the two periods without the denuder was termed NO_2^+. The parameter NO_y was defined as:

$$NO_y = NO_2^+ - NO_2$$

NO_y was, therefore, a measure of the hourly average concentration of interferents removed by the denuder. One-hour average concentrations of NO_2, NO_2^+ and NO_y were calculated and listed with a Kaye Digistrip III data system. No difference with or without the denuder was expected for atmospheric NO. Accordingly, one hour average NO values, based on the mean of four, 15-min. averages, were also calculated by the data system. No effort was made to develop a denuder for peroxyacetyl nitrate (PAN). Since this

---

* The solution is described in Appendix A.

Table 1. Sampling Design for Fall SCAQS Study

Sampler	Collection Medium	Flow Rate, Lpm	Samples/ Day	Species Measured
Annular Denuder[a]	$CO_3^=$-glycerol	17	5	HONO, HNO_3, HCl
Annular Denuder[a]	Citric acid-glycerol	17	5	NH_3
TECO NO_x Box		0.6	24[b]	NO, NO_2, NO_y
Dasibi O_3 Monitor		1.0	continuous	O_3
EG&G Hygrometer		1.5	continuous	R.H., T

a.   Two denuder sections in tandem.

b.   The analyzer is switched every 15 min. to sample with or without a denuder. One hour average values of NO, NO_2 and NO_y are calculated and listed with a data logger.

﹣

Table 2. Analytical Strategy for Six Day Fall SCAQS Study

Collection Medium	No. Samples	NH_4^+	NO_2^-	NO_3^-	Cl^-
			Number of Determinations		
Citric acid/glass	70[a]	80			
$CO_3^=$ glycerol/glass	70[a]		80	80	80
Totals:	140	80	80	80	80

Total Determinations: 320

a.   Two samples per sampling period plus ten field blank samples.

Figure 4.

NO_x Analyzer Strategy for Measuring NO_2 and NO_y

LONG BEACH SCAQS

CO_3^- CO_3^-

NO_2

NOx
BOX

NO_2^+
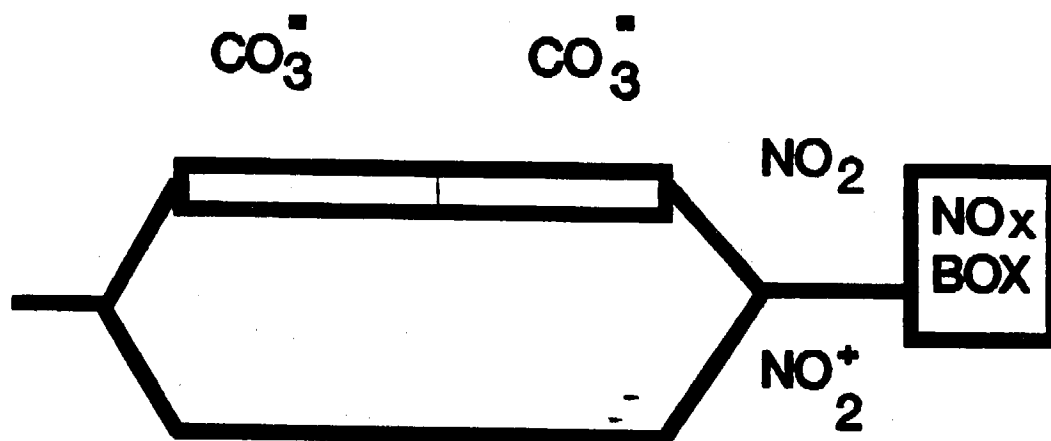
$$NO_2^+ - NO_2 = NO_Y$$

$$NO_Y = PAN + HONO + HNO_3 + OTHERS?$$

material, if present, would represent a 100% positive interferent in NO_2 measurement (2), correction of NO_2 values may be necessary.

The CA was calibrated at the sampling site with a cylinder of NBS certified 47.5 ppm NO in N_2*, with quantitative dilution to concentrations <1 ppm. For range 0.5 ppm (500 ppb) full scale, the calibration, with NO in ppb, was:

$$mV = 0.0146 \ [NO] + 0.144$$

The efficiency of the molybdenum converter was assessed at the sampling site by a gas phase titration procedure in which NO is converted to NO_2 with O_3, and the instrument response to NO_2 passing through the converter is compared to that for the starting NO, analyzed directly. The resulting NO_2 calibration, with NO_2 in ppb, was:

$$mV = 0.0139 \ [NO_2] + 0.107$$

Comparing responses for NO and NO_2 indicates about 95% converter efficiency. No correction for the small difference in response of NO and NO_2 was made, consistent with the usual practice when operating CA units.

C. ## Nitrous, Nitric and Hydrochloric Acid Measurement

Sampling of HONO, HNO_3 and HCl was done using two, CO_3^--glycerol coated annular denuders in tandem. Each denuder was 217 mm long and 28 mm in outer diameter. The concentric rod forming the annulus within each denuder was recessed at the inlet end by about 25 mm, intended as a flow straightener, since laminar flow is essential. The recessed section has interior surfaces coated with Teflon. The two denuders were joined with a threaded coupler using a Teflon gasket. Similarly, threaded couplers were used to attach the cyclone and vacuum source. The technique used for denuder coating is given in Appendix A. Sampling rates were maintained with a Tylan mass flow controller. Flow rates were set to 17 Lpm against a Fisher-Porter rotameter (50 Lpm full scale) attached to the cyclone inlet at the start of each sampling period. The rotameter was previously calibrated against a dry test meter. Flow rates were checked at the end of each sampling period and mean flow rates used to calculate sampling volumes. Flow rate change was ≤10%, measured with the rotameter. Results were uncorrected for pressure or temperature change. Coarse particles were excluded with a Teflon-coated glass cyclone, internal volume 75 mL (University Research Glassware, Carrboro, NC).

In unsponsored preliminary trials performed in parallel with summer SCAQS measurements at Long Beach, we sampled in parallel with two annular denuders coated with Na_2CO_3-glycerine. One of the two units was preceded by an FEP Teflon-coated glass cyclone (volume 75 mL). The second unit sampled directly into the annular denuder.

---

* The NO cylinder was provided by the General Motors Research Laboratory study participants.

-14-

Both units had backup annular denuder sections to correct for artifactual HONO. <u>Figure 5</u> compares the NO_2^- recovered from the front denuder of Sampler 5 (with cyclone) and that for Sampler 4, without the cyclone, uncorrected for sampling artifacts. The results are highly correlated (r=0.96) with the denuder preceded by the cyclone exhibiting higher NO_2^-. Based on ratios of means, the unit with the cyclone (Sampler 5) showed, on average, 8% higher values. At the mean, this corresponded to 0.1 $\mu g/m^3$ greater NO_2^-. The difference between samplers with and without a cyclone was judged insignificant. Since the accurate measurement of HNO_3 and HCl with the annular denuder required removal of coarse particulate nitrate and chloride, the annular denuder in the present study employed the Teflon-coated glass cyclone.

D.   <u>Ammonia Measurement</u>

Ammonia was measured with the ADM employing two denuders in tandem, both coated with citric acid-glycerol as detailed in Appendix B. Flow rates were set and measured as described in section C, above. The sampling design permitted an assessment of collection efficiency under field conditions. A Teflon-coated glass cyclone, internal volume 75 mL, (University Research Glassware, Carrboro, NC) preceded the sampler to exclude coarse (i.e. >2 or 3 μm) particles. Loss of NH_3 within this cyclone was not assessed, but was assumed to be no greater than that found for HNO_3 (i.e. <10% at 50% R.H., ca. 35% at 80% R.H.) in a prior study (6,23).

Immediately following each sampling period, the two denuders were separated and extracted as described in Appendix B. The specific ion electrode was calibrated before each sample set.

E.   <u>Ozone, Temperature and Relative Humidity Measurement</u>

Ozone was monitored continuously by a UV absorption method (DASIBI Model 1003 AH). Ambient temperature and relative humidity were measured continuously with an RTD (platinum) thermo-couple and dew-point measurement (EG&G Model 911).

The DASIBI response to ozone was established with an ozone generator (MEC-1000) whose output had been verified with the ARB's DASIBI O_3 transfer standard. The EG&G RH-T monitor was factory calibrated. Periodic comparisons were made of the instrument RH values with those using a sling psychrometer. The comparison (<u>Figure 6</u>) indicates good correlation between methods, with a ratio of mean results EG&G/psychrometer of 0.94.

Figure 5.

NO$_2^-$ ON DENUDER WITH VS. WITHOUT A
TEFLON-COATED GLASS CYCLONE
SUMMER SCACS
LONG BEACH

$Y = 0.66 + 0.71 \; X$
$r = 0.96$

Figure 6.

SLING PSYCHROMETER VS. EG&G
RELATIVE HUMIDITY MEASUREMENT

Y = 10.7 + 0.79 X
r = 0.855

EG&G - %RH

SLING PSYCHROMETER - %RH
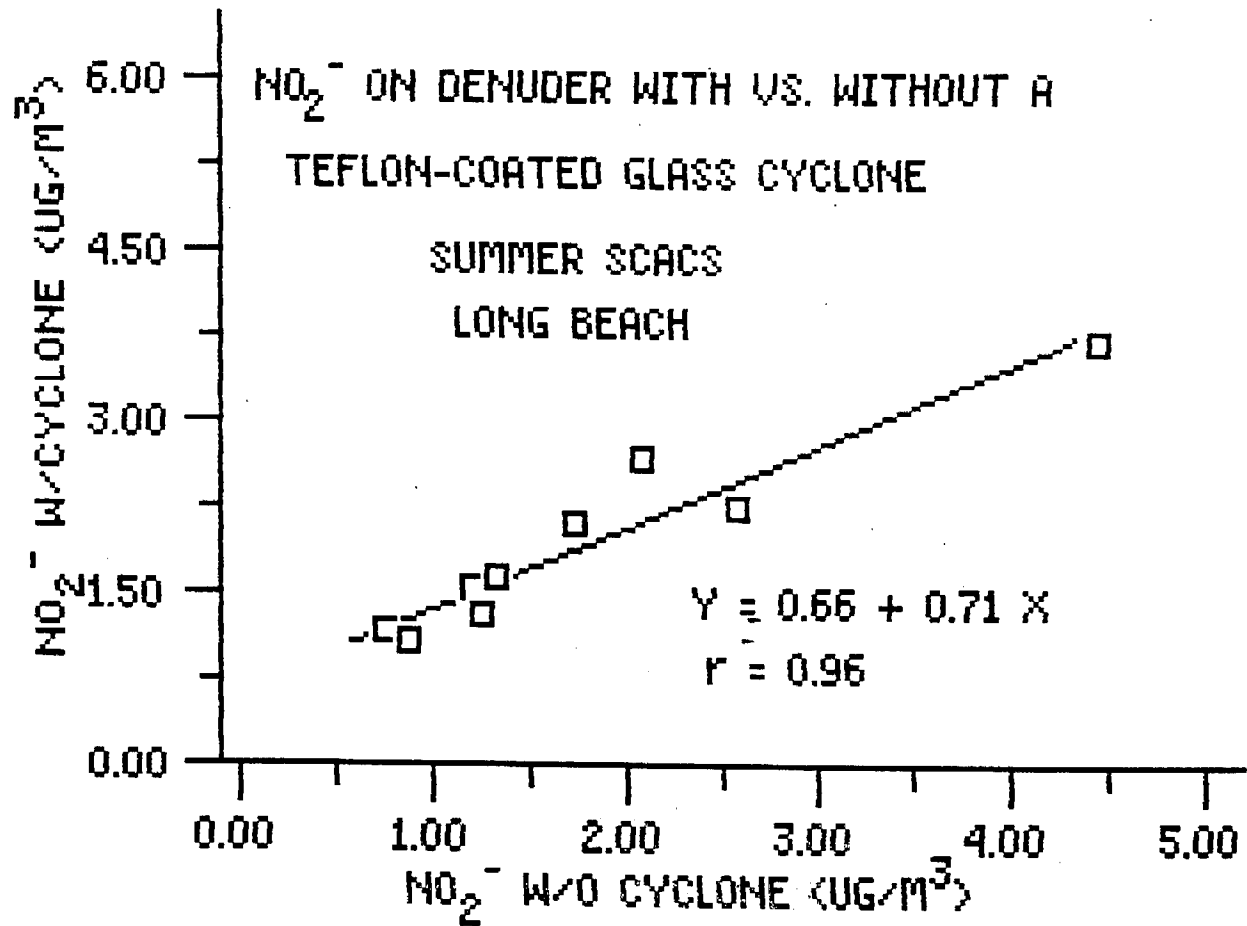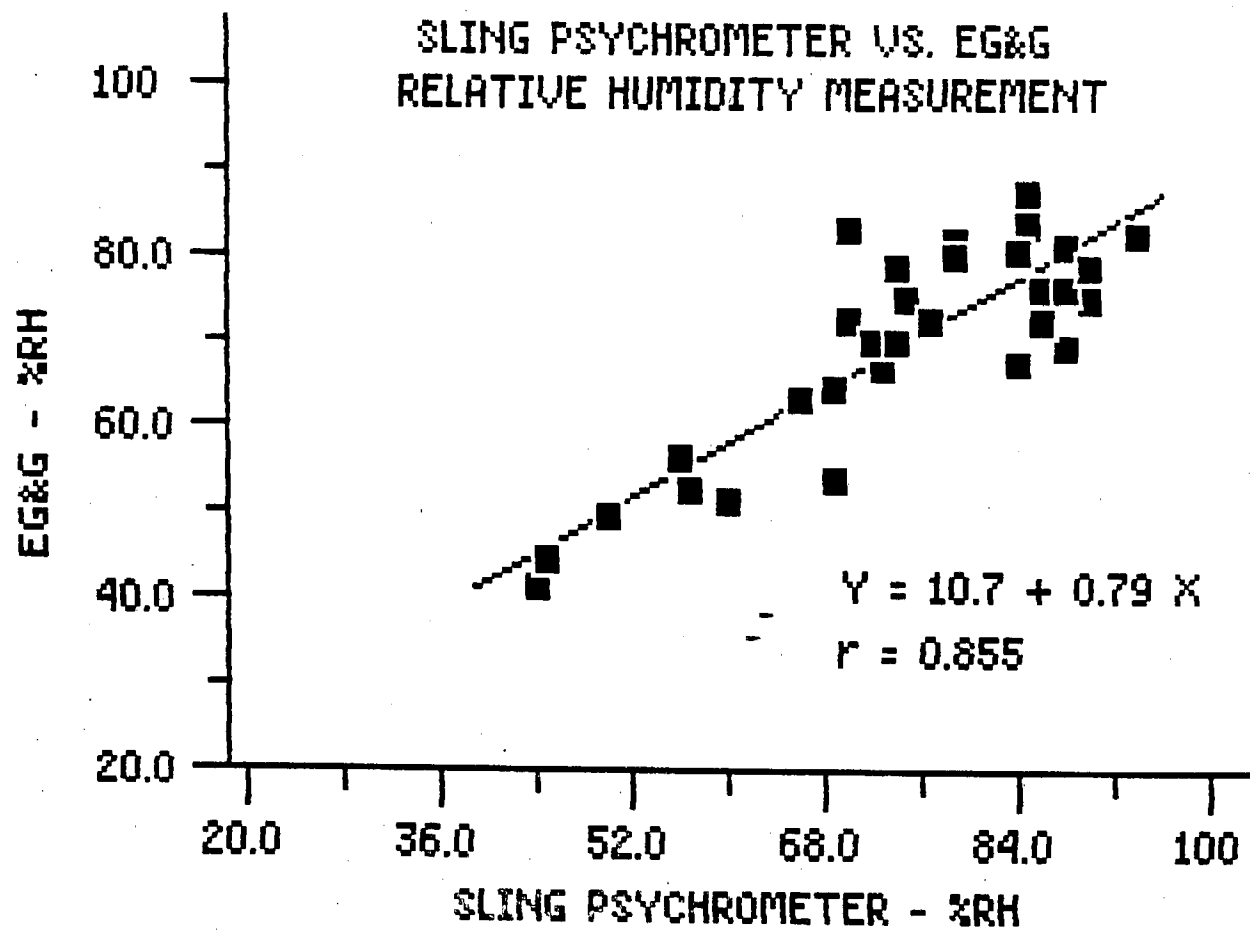
IV. QUALITY ASSURANCE AND ATMOSPHERIC RESULTS

A. Quality Assurance for Principal Species

Precision for NH_4^+ analyses was assessed by analyzing, in duplicate, five front denuder and five rear denuder atmospheric samples. The re-analyses were done on the same day to minimize sample decomposition, but following completion of the initial analysis of the ten samples. The median C.V. for the front samples was 1.5% (range 0.6-3.9%), and for the rear samples, 14.6% (range 1.4 to 204%). The poorer precision with the back denuder reflected the relatively low concentration of NH_4^+ in these samples. The efficiency of a single, 30-cm, citric acid-coated denuder tube was assessed by comparing the blank-corrected NH_4^+ concentrations measured with the tandem collectors. For 30 sampling periods the mean NH_3 (as NH_4^+) for the front and rear denuders was 4.94 and 0.12 $\mu g/m^3$, respectively.* This indicates an efficiency of about 97%.

The accuracy of the NH_4^+ determinations was assessed by analyzing standard NH_4^+ solutions prepared independently and supplied as unknowns. The results are given in Table 3 and show accuracy within 4% in the range 1-4 $\mu g/mL$, but poor accuracy at 0.5 $\mu g/mL$. However, for the 30 front denuder samples collected in Long Beach, only four were <1.0 $\mu g/mL$. Based on this evaluation, the influence of analytical error was judged to be minor.

Ammonium ion determinations with the SIE were compared to those using an automated indophenol blue procedure (26), as carried out by Environmental Monitoring & Services, Inc. (EMSI). For this purpose, aliquots from the extracts for samples collected on Julian day 344 were analyzed by EMSI after about three months refrigerated storage. Because of the substantial delay in analysis, the EMSI results are more likely to represent minimum NH_4^+ concentrations for the samples. As shown in Figure 7, the EMSI results averaged about 40% higher than those by the SIE method, in spite of the time delay.

The precision of the anion analyses was assessed by duplicate analysis of five front and five rear denuder sections, analyzed twice on successive days. The median C.V. values are given in Table 4. The precision for analyses done on rear denuders was expected to be poorer because of lower concentrations. Only with Cl^- was this observed.

The accuracy of the ion chromatographic analyses for NO_2^-, NO_3^- and Cl^- was not assessed in the present study. A prior comparison of NO_2^- analyses by the present analyst and equipment with those by another analyst with a second IC unit and independently prepared standards showed excellent agreement (6). Extraction and IC analysis of Nylon filters spiked with known amounts of NO_3^- showed recoveries of 97-98% for samples containing ≥ 67 μg NO_3^- (8). In

---

* Seventeen of the rear denuder results were below the limit of detection (L.D.). For purposes of this calculation, a concentration of L.D./2 was assumed for each of these samples.

Table 3. Analysis of Independently Prepared Ammonium Ion Standard Solutions

True Concentration, μg/mL	Found, μg/mL	% Error
0.50	0.21	-57
1.00	0.98	-2
2.00	1.94	-3
4.00	3.86	-3.5

Table 4. Median Coefficients of Variation (%) for Atmospheric Samples on Front and Rear Carbonate-Glycerol-Coated Denuders[a]

Species	Front	Rear
Cl^-	3.5	15.4
NO_2^-	8.9	7.8
NO_3^-	9.2[b]	9.2

a.   Except as noted, n=5

b.   n=4

Figure 7.

Comparison of NH_4^+ Analysis on Split Samples Using a Selective Ion
Electrode (AIHL) and an Automated Colorimetric (EMSI) Procedure

$$Y = -2.21 + 1.43 \; X$$
$$r = 0.95$$
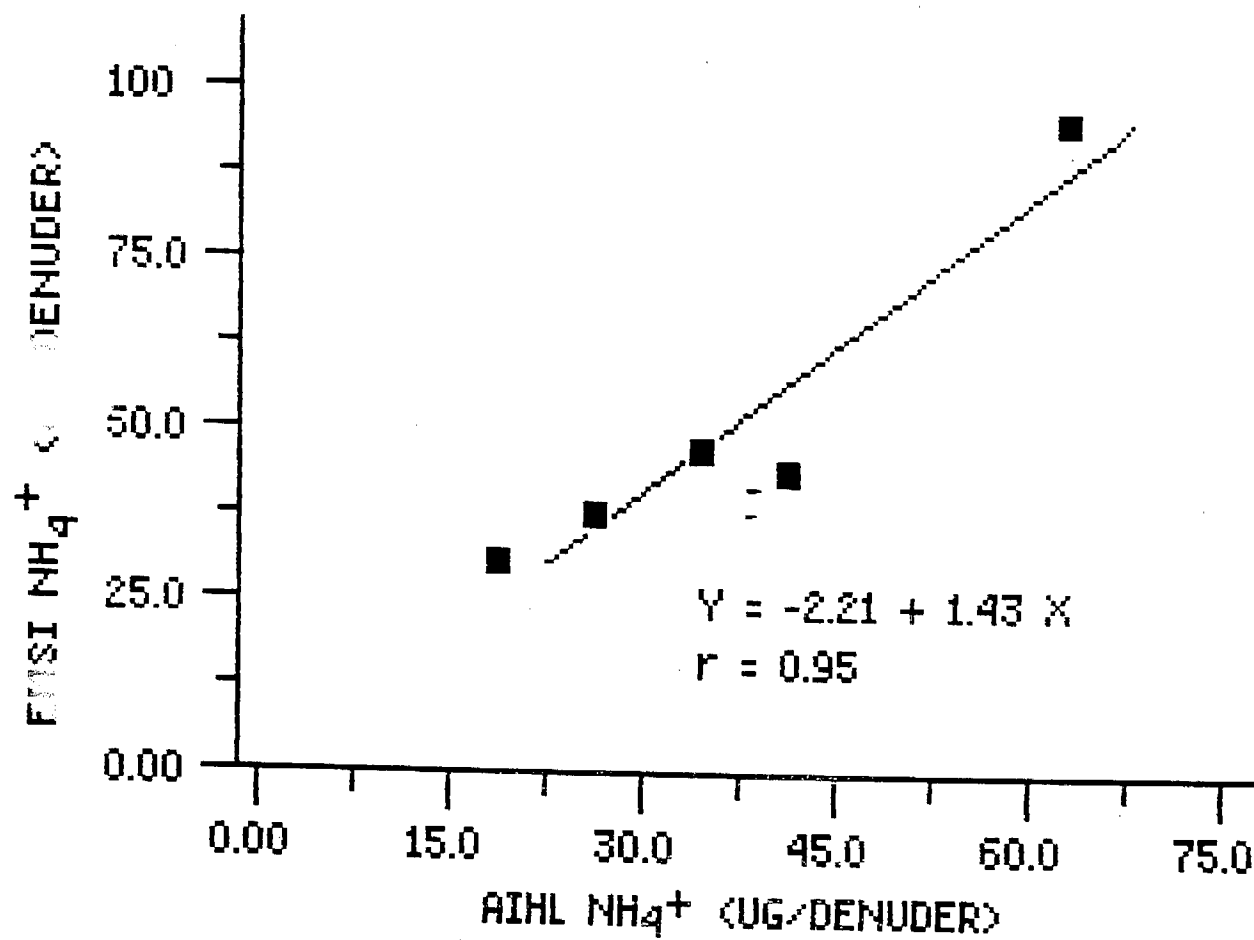
the present study, results above the limit of detection for NO_3^- are reported for blank-corrected samples averaging 20 μg (range 4 to 68 μg). Chloride results above the limit of detection are reported for blank-corrected samples averaging 23 μg (range 10-50 μg).

The degree of loss of NO_2 passing through the $CO_3^=$ denuder ahead of the chemiluminescent NO_x analyzer was expected to be slight, based on published results with CO_3^--coated annular denuders (11) as well as our own prior study (6). Nevertheless, this was checked for both one and two 30-cm, 6 mm I.D. denuder tubes in series, using 60 ppb NO_2 in synthetic air humidified to 50 ± 5% R.H. To insure the absence of HNO_3, the dilute NO_2 in humidified air passed through two Sartorius Nylon filters. Immediately before entry to the 3-way solenoid valve, the NO_2 stream passed through a single CO_3^--glycerol-coated denuder. Thus HNO_3^- and HONO-free NO_2 in air entered the 3-way valve. Trials using either one or two denuder tubes in series showed no measurable (i.e. <0.5%) change in NO_2 analyzer response with and without the denuder in line. Thus NO_2 loss within the denuder was judged to be negligible.

Field blanks were obtained by five dual ADM samplers for NH_3 and for HONO, HNO_3 and HCl, operating the samplers for 30 seconds, extracting, storing and analyzing the blanks together with the atmospheric samples. The field blank results are summarized in Table 5. Limits of detection, calculated from twice the standard deviation of these blanks, are also shown. Nitrites and chloride on the front denuder showed relatively high blanks. Of greatest concern was the poor precision of the NO_2^- blank value, which showed a C.V. of 41%, and a corresponding limit of detection of 1.1 $\mu g/m^3$ for a 4-hr sample. For the thirty sampling periods, the front and rear denuders generally yielded 5 or 6 samples below the L.D. for each of the species NO_2^-, NO_3^- and Cl^-. With NH_4^+, all front denuder results were above the L.D., while the rear denuder provided 14 samples below the L.D.

B. Atmospheric Nitrous, Nitric and Hydrochloric Acid Concentrations at Long Beach

Table 6 lists results for the concentrations of atmospheric NO_2^-, NO_3^- and Cl^- for each of the two tandem annular denuders for each sampling period. Nitrous acid concentrations were estimated by subtracting rear from front denuder NO_2^- values as discussed in Section IIC. The correction represented, on average, 8.5% of the NO_2^- retained on the front denuder. The measured four- or six-hour average HONO concentrations ranged up to 27 $\mu g/m^3$ (as NO_2^-) or 14 ppb. This compares to <1 hour maxima up to 10 ppb observed by UC (Riverside) personnel at El Camino College (Torrance) using dual optical absorption spectrometry (24). Appendix C is a listing of HONO, HNO_3 and HCl results, including standard deviations, for inclusion in the SCAQS data base. The standard deviations are based on the analytical precision observed with atmospheric samples, with allowance for the measured concentration range.

Figures 8-13 show diurnal variations for HONO on each intensive sampling day. HONO concentrations are plotted in ppb to facilitate

Tab.. 3.   Field Blanks and Limits of Detection[a]

Species	Front Denuder			Rear Denuder		
	Blank (μg/filter)	L.D. (μg/filter)	L.D. (μg/m³)[b]	Blank (μg/filter)	L.D. (μg/filter)	L.D. (μg/m³)[b]
Cl^-	5.74 ± 1.36	2.7	0.6	2.30 ± 0.75	1.5	0.4
NO_2^-	5.80 ± 2.40	4.8	1.1	1.59 ± 0.36	0.7	0.2
NO_3^-	3.20 ± 1.40	2.8	0.7	-0-	0.5[c]	0.1[c]
NH_4^+	1.61 ± 0.29	0.6	0.1	1.60 ± 0.25	0.5	0.1

a.   Mean and standard deviations for five field blanks. Except as noted, limits of detection set equal to two standard deviations of the field blank. Results for Cl^-, NO_2^- and NO_3^- by ion chromatography. Results for NH_4^+ by specific ion electrode.

b.   Based on a 4-hour sampling period at ca. 17 Lpm.

c.   Estimated values.

TABLE 6. HONO, HNO3 AND HCl RESULTS AT LONG BEACH

ID	STARTDATE JULIAN	START TIME	FT NO2- UG/M3	RR NO2- UG/M3	HONO UG/M3*	HONO PPB	FT NO3- UG/M3**	RR NO3- UG/M3	FT CL- UG/M3***	RR CL- UG/M3
S011	11/11/87	0000	10.48	0.93	9.55	5.09	0.35	<0.07	<0.4	0.51
S012		0600	5.87	1.12	4.75	2.53	1.93	<0.1	3.00	0.42
S013	(315)	1000	<1.1	<0.2	<1.1	<0.6	8.54	0.62	7.36	3.44
S014		1400	3.11	0.48	2.63	1.40	9.78	<0.1	5.96	2.89
S015		1800	10.24	0.99	9.24	4.92	0.71	<0.1	0.85	1.75
S021	11/12/87	0000	18.91	0.98	17.94	9.55	<0.5	0.37	<0.4	0.64
S022		0600	11.32	<0.2	11.32	6.03	<0.7	<0.1	<0.4	1.29
S023	(316)	1000	3.25	0.43	2.82	1.50	13.18	0.79	10.61	0.22
S024		1400	1.81	1.00	0.80	0.43	10.05	1.08	5.08	0.81
S025		1800	13.81	0.89	12.91	6.88	10.21	0.38	4.31	0.60
S031	11/13/87	0000	11.76	1.09	10.68	5.69	4.27	0.37	4.98	0.17
S032		0600	8.84	0.48	8.36	4.45	3.71	<0.1	2.13	0.54
S033	(317)	1000	<1.1	<0.2	<1.1	<0.6	9.05	1.71	10.56	0.79
S034		1400	<1.1	<0.2	<1.1	<0.6	2.11	1.25	3.80	0.52
S035		1800	<1.1	<0.2	<1.1	<0.6	1.49	<0.1	2.18	1.81
S041	12/3/87	0000	28.83	1.90	26.93	14.34	2.12	0.81	1.51	1.28
S042		0600	26.29	1.95	24.34	12.96	0.64	0.82	0.84	0.63
S043	(337)	1000	8.48	1.69	6.79	3.62	12.90	1.41	9.59	1.57
S044		1400	6.47	1.67	4.80	2.55	14.71	1.75	6.63	1.18
S045		1800	18.27	1.76	16.51	8.79	0.57	0.24	1.00	<0.3
S051	12/10/87	0000	<0.7	<0.13	<0.7	<0.4	<0.5	<0.1	<0.4	<0.3
S052		0600	****	1.50	****	****	1.48	1.38	<0.6	0.50
S053	(344)	1000	4.73	1.49	3.24	1.72	10.79	1.74	7.22	0.58
S054		1400	6.70	1.25	5.45	2.90	7.21	1.73	5.96	0.83
S055		1800	20.65	2.43	18.22	9.71	<0.5	0.78	<0.4	0.93
S061	12/11/87	0000	18.01	1.61	16.40	8.73	<0.5	0.56	<0.4	0.76
S062		0600	16.79	2.79	14.01	7.46	<0.7	2.05	<0.6	1.99
S063	(345)	1000	7.90	1.25	6.65	3.54	15.54	1.37	10.68	1.12
S064		1400	9.51	1.54	7.98	4.25	4.71	1.00	2.95	0.58
S065		1800	35.58	3.13	32.45	17.28	<0.5	1.13	<0.4	1.00

* as NO2-

** used as a measure of HNO3

*** used as a measure of HCl

**** not determined

Figure 8.

HONO VS. TIME
JULIAN DAY 315

TIME OF DAY (PST)

Figure 9.

HONO VS. TIME
JULIAN DAY 316

TIME OF DAY (PST)

Figure 10.

HONO VS. TIME
JULIAN DAY 317

Figure 11.

HONO VS. TIME
JULIAN DAY 337

Figure 12.

HONO VS. TIME
JULIAN DAY 344

TIME OF DAY (PST)

Figure 13.

HONO VS. TIME
JULIAN DAY 345

TIME OF DAY (PST)
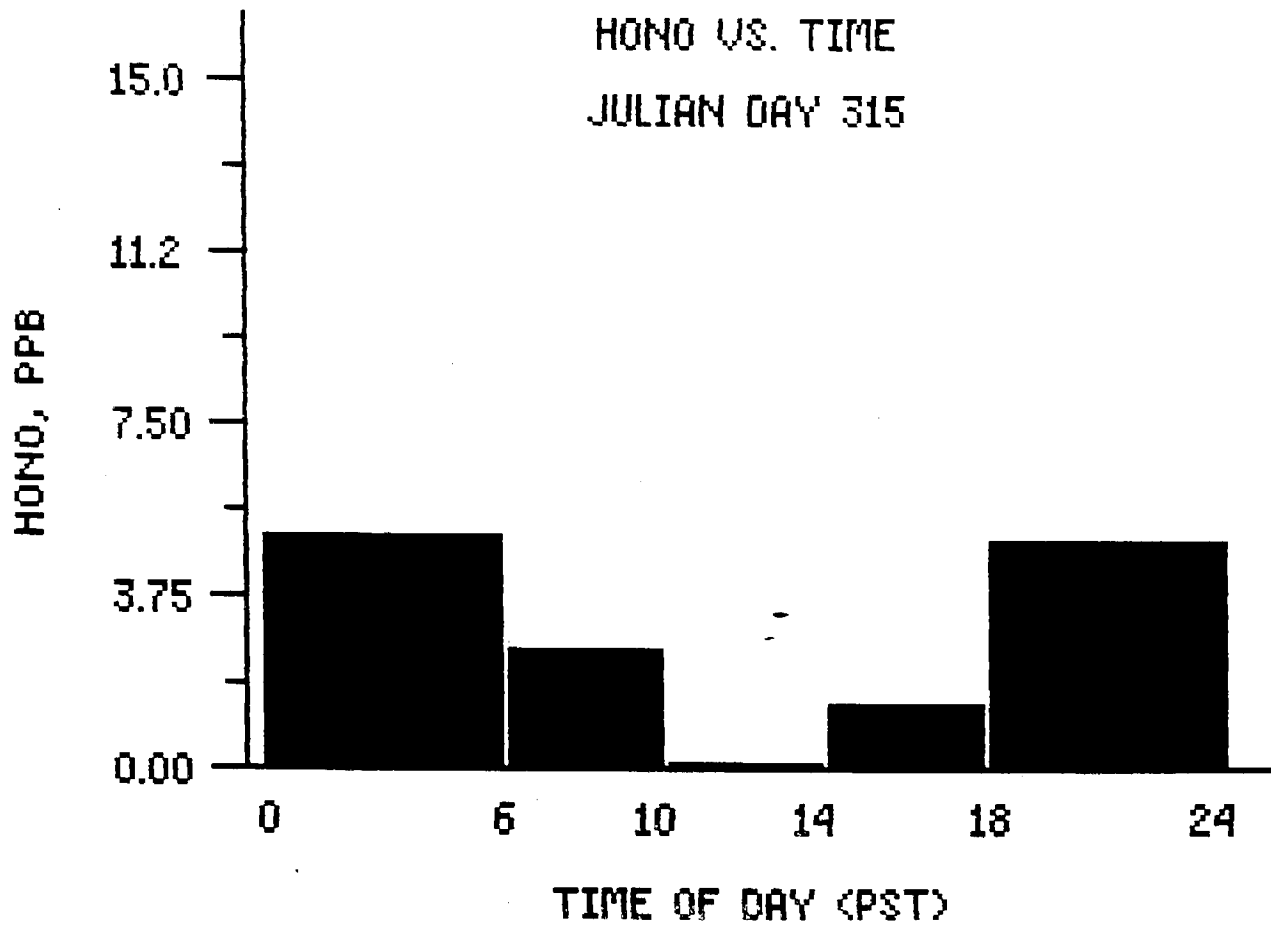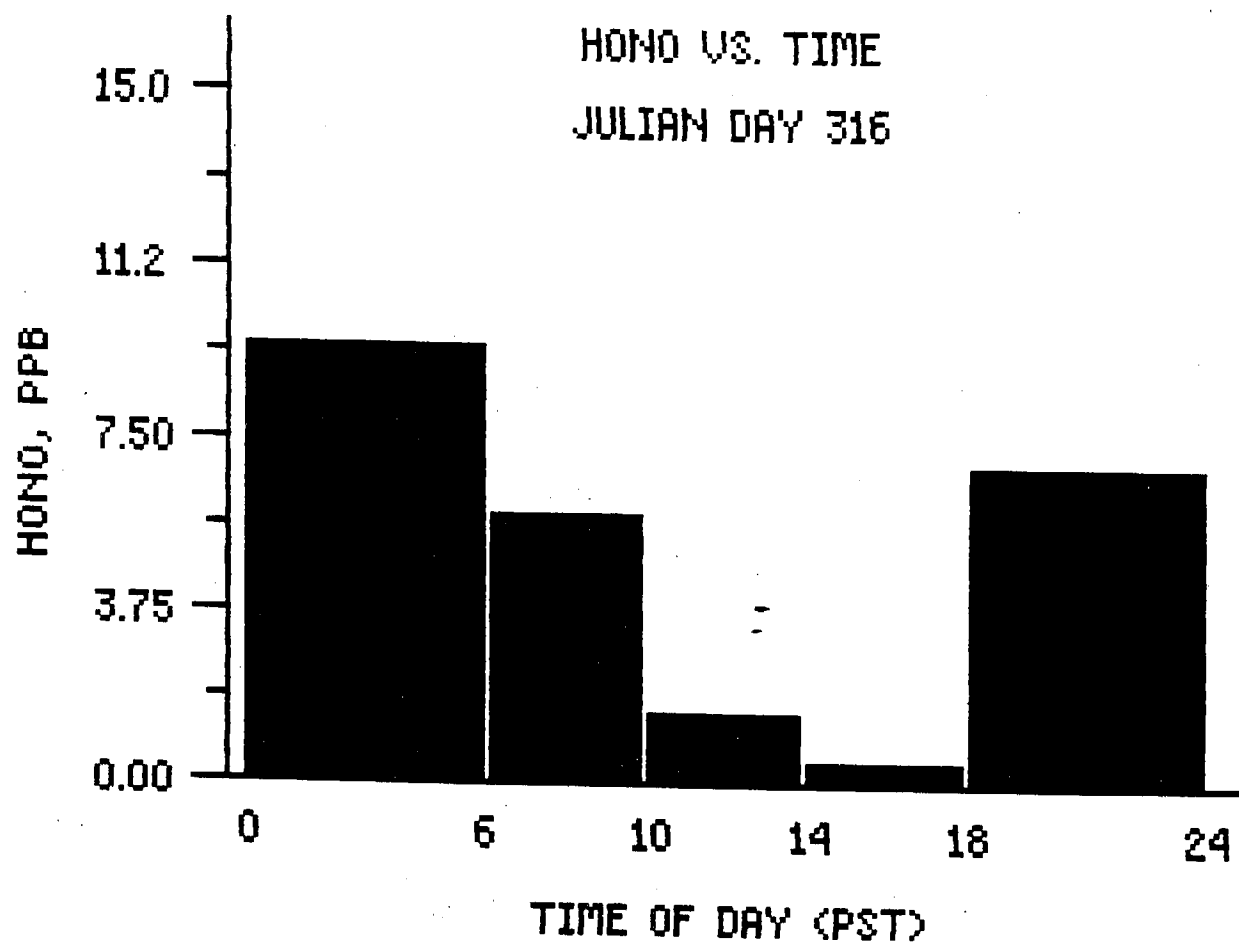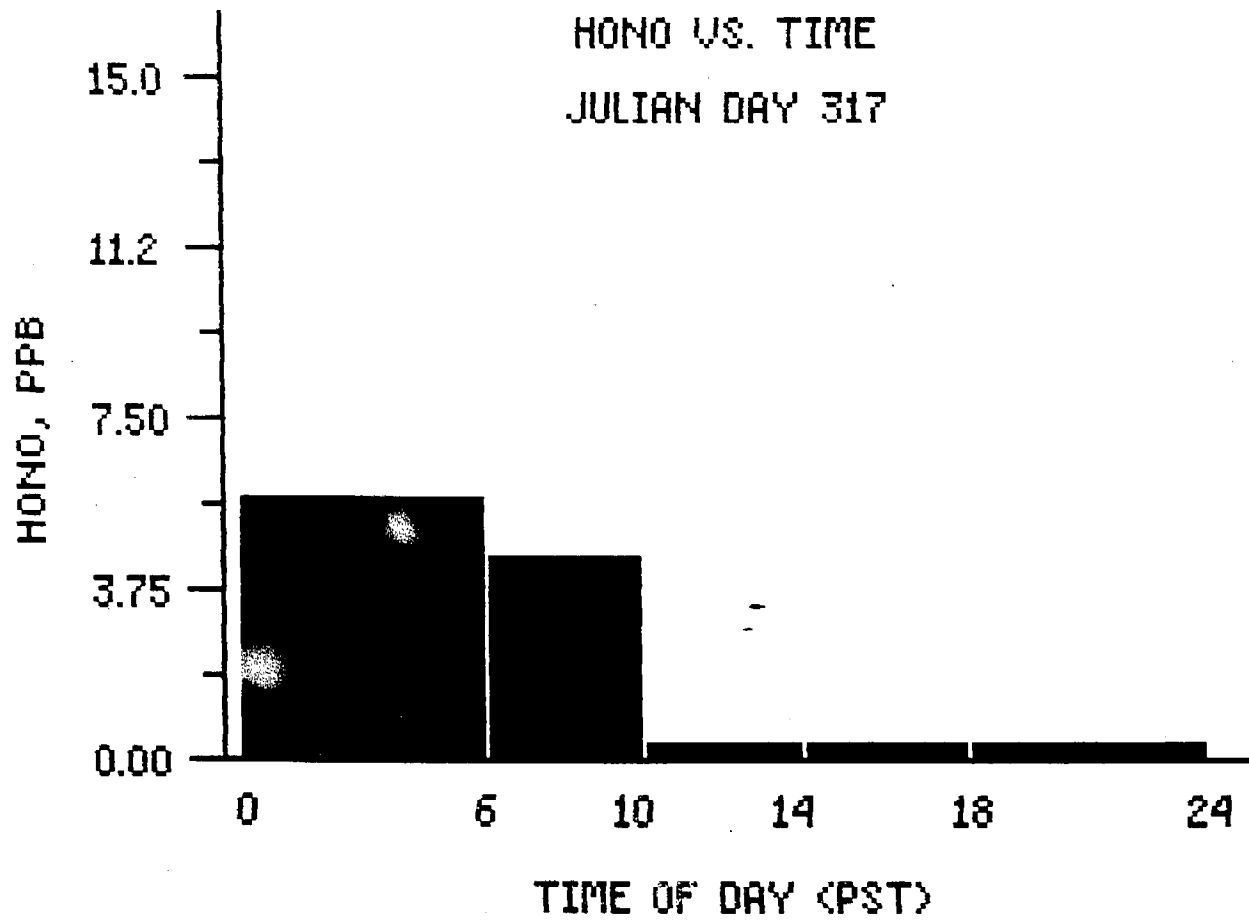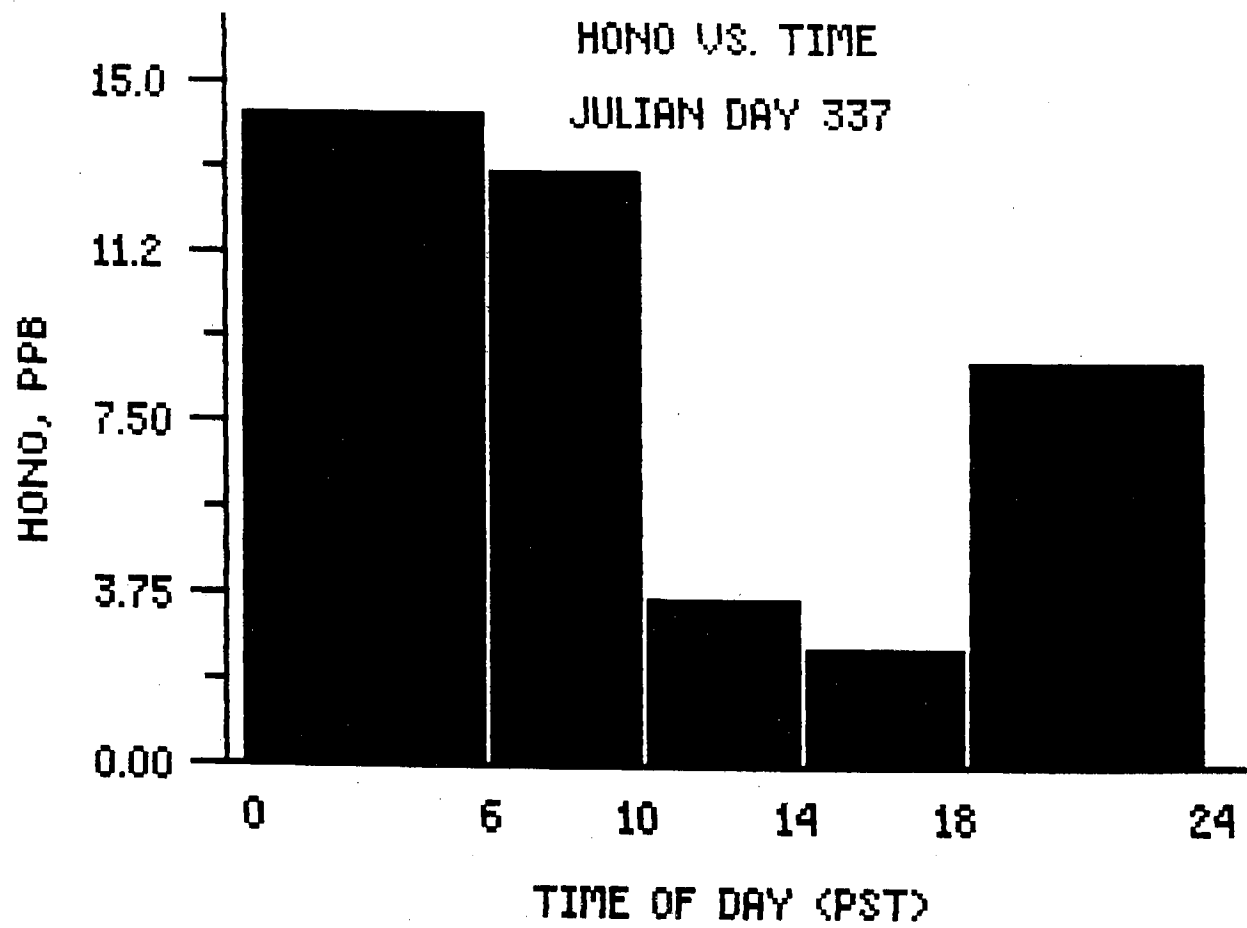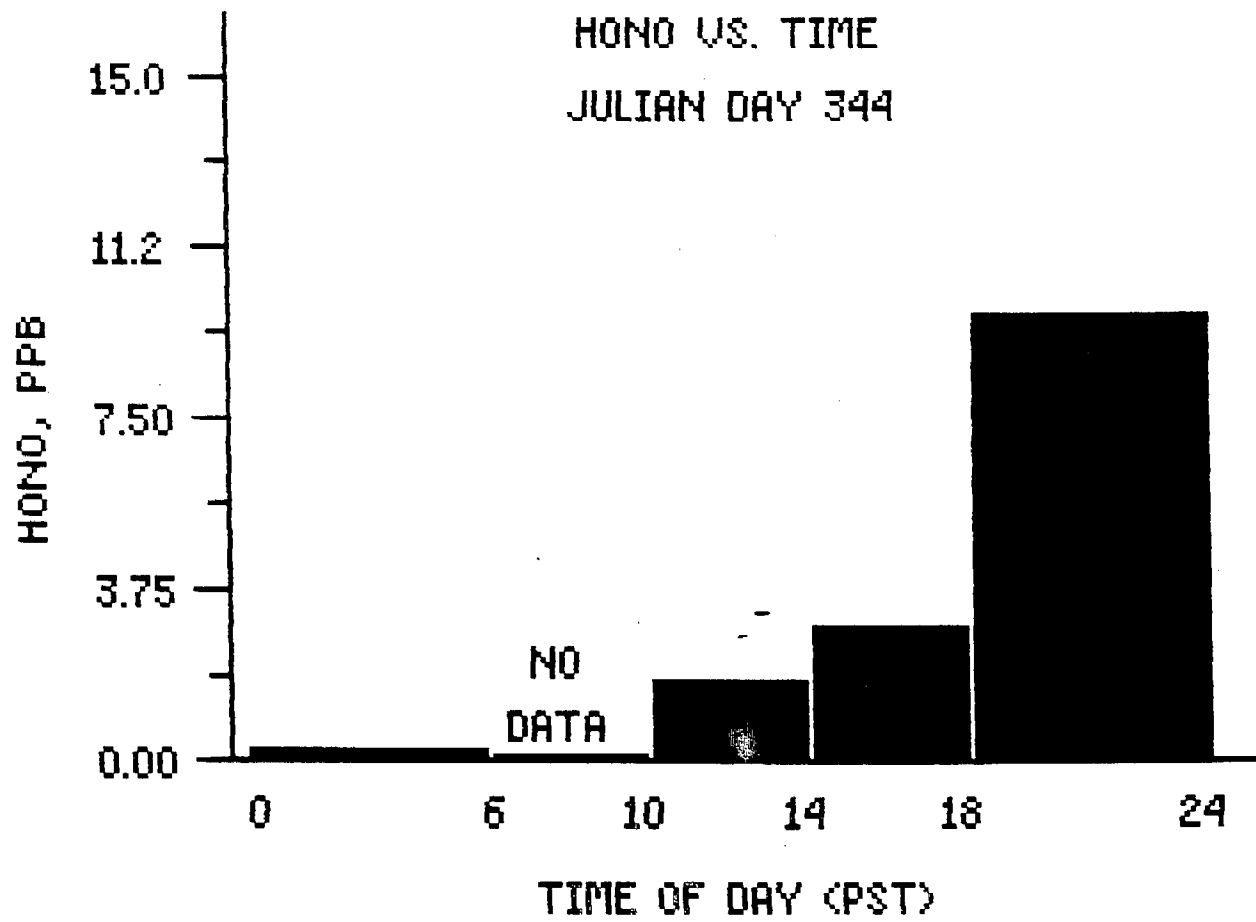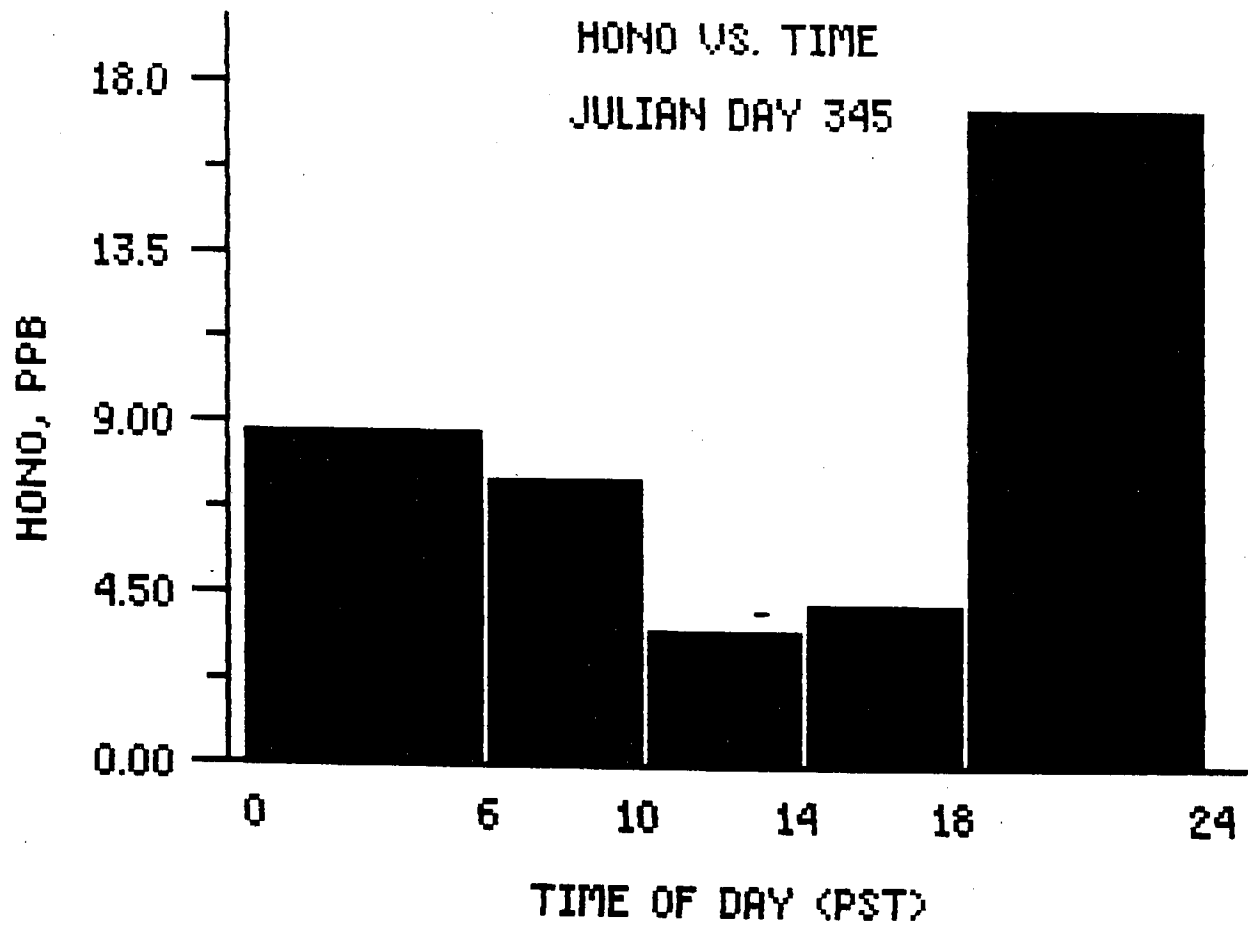
subsequent method comparisons (not included in this report). The diurnal maxima occurred during the period midnight to 0600 hours, when photochemical decomposition of HONO would be minimized. However, daytime concentrations up to 8 $\mu g/m^3$ (4 ppb) were observed, much higher than would be expected. This suggests that positive errors (e.g. formation of artifact HONO) might be a measurable source of error. This can best be assessed by comparing results with those obtained by simultaneous spectroscopic measurements. Such results are currently unavailable. Analytical error appears unlikely to have caused elevated HONO results; nitrite in a carbonate-bicarbonate buffer extract was shown to decay almost completely to zero concentration in 30 days at room temperature but showed little if any change at 5°C (6).

The present HONO results may be compared to those obtained in June and July 1987 at Long Beach. Table 7 includes a data set for a sampler with a preceding cyclone. The Fall SCACS HONO concentrations are markedly higher, both at night and day. Whereas nighttime HONO maxima were always seen in the Fall SCAQS, on 7/14 and 7/15, measured HONO values were highest during daylight hours. Such results are judged to be probably in error, perhaps reflecting inadequate correction for the partial conversion of PAN to NO_2^-.

Nitric acid was measured by NO_3^- recovered from the front annular denuders. The concentration recovered from the rear denuder was on average, 14% of that on the front. However, for single sampling periods, the percentage retained on the back denuder was as high as 93% of that on the front. As discussed in Section II, several potential sources exist for NO_3^- on the rear denuder. Accordingly, no correction of results was attempted. Figures 14-19 show diurnal variations for HNO_3 on each intensive sampling day. As usual, HNO_3 levels were highest in midday, with levels up to 15.5 $\mu g/m^3$ (6.0 ppb).

At 25°C, the dissociation constant for pure NH_4NO_3 is 28 $(ppb)^2$ (19). At relatively low concentrations, NH_3 was not expected to influence the observed HNO_3. Figure 20 plots HNO_3 against NH_3 concentrations. The general trend is consistent with high HNO_3 when NH_3 is low, and vice versa. However, NH_3 levels tended to be high at night when HNO_3 formation is probably less rapid, making the trend suggested by Figure 20 possibly misleading.

The concentration of HCl can be estimated from the denuder collection of acidic, gaseous Cl^-, since HCl is likely to be the dominant contributor to such Cl^-. On average, 83% of the total collected Cl^- was on the front denuder, compared to 86% for NO_3^-. Collection efficiency for HCl would be expected to be somewhat greater than for HNO_3 because of the higher diffusion coefficient for the smaller molecule. The results suggest that species other than HCl can contribute to measured Cl^-. Based on front denuder results only, HCl concentrations up to 11 $\mu g/m^3$ as Cl^- were observed, with a consistent diurnal maximum in the period 1000-1400 hours. Figure 21 shows a typical diurnal pattern. The relatively high diurnal maxima contrast with prior results obtained at Claremont (8) and Riverside (20) for which a 4 or 6-hr maximum of 3

Table 7. **Summer SCAQS HONO Concentrations at Long Beach ($\mu g/m^3$ as NO_2^-)**

Date	Time Period (PDT)[a]				
	01-06	06-10	10-14	14-18	18-01
6/19/87	2.82	1.40	0.85	1.47	1.85
6/24/87	2.27	2.56	1.11	1.41	1.42
6/25/87	1.75	1.95	0.86	0.96	1.73
7/13/87	5.28	5.78	2.09	2.51	1.79
7/14/87	1.26	2.98[b]	2.17[b]	1.49	1.31
7/15/87	0.93	0.0	2.35[b]	1.11	0.99

a. Samples collected with a CO_3^--glycerine coated annular denuder with preceding cyclone. Results corrected for NO_2^- on a backup denuder.

b. Result considered suspect.

Figure 14.
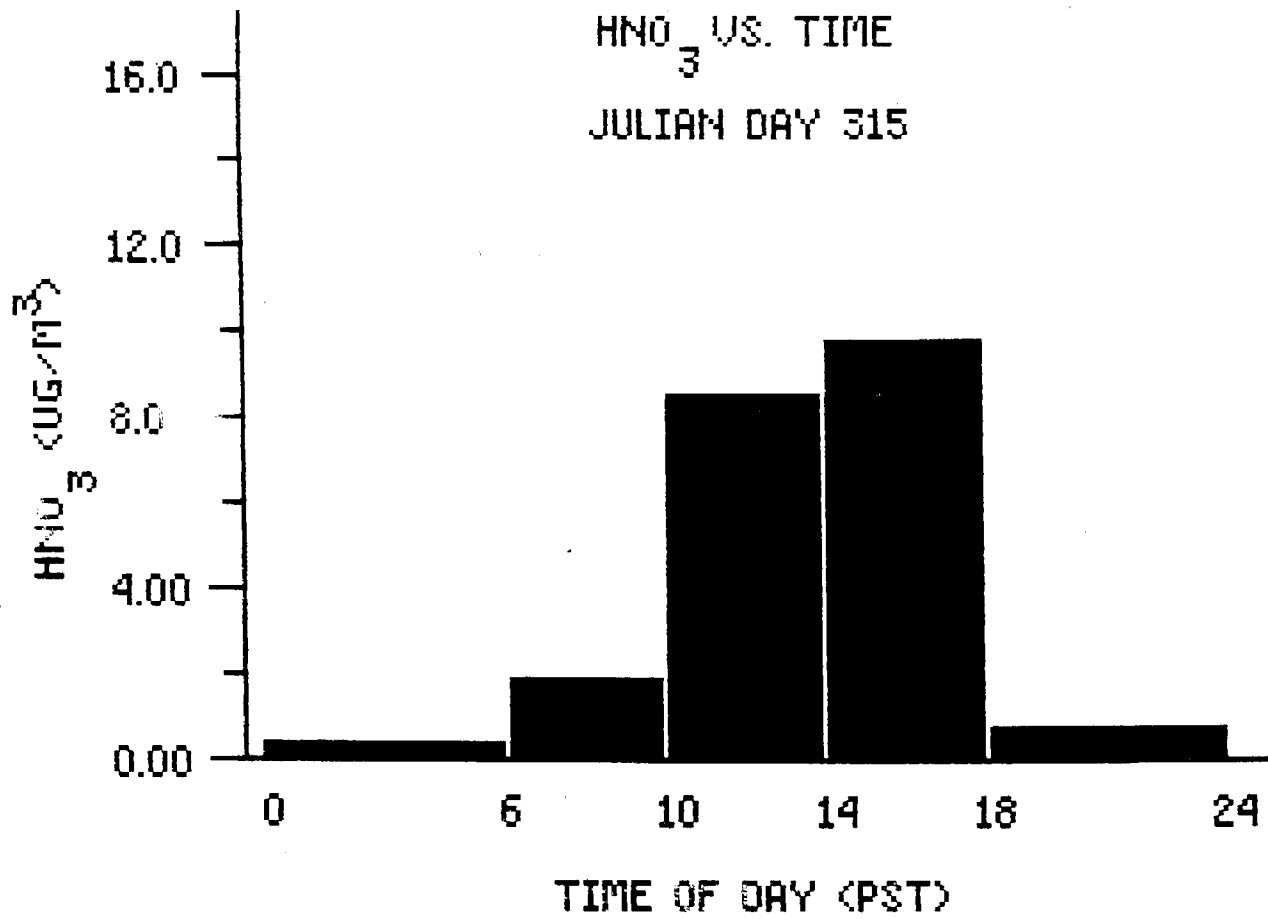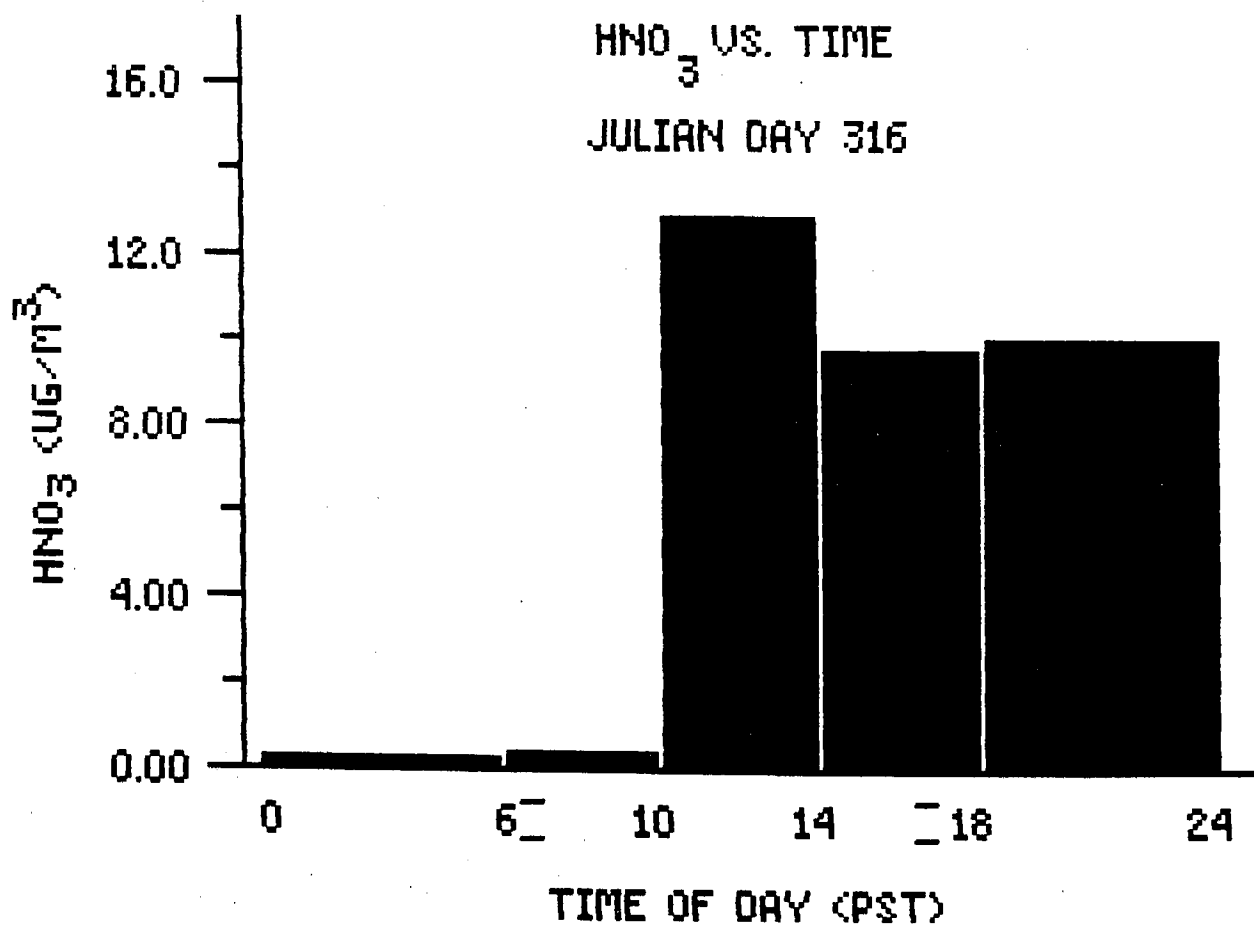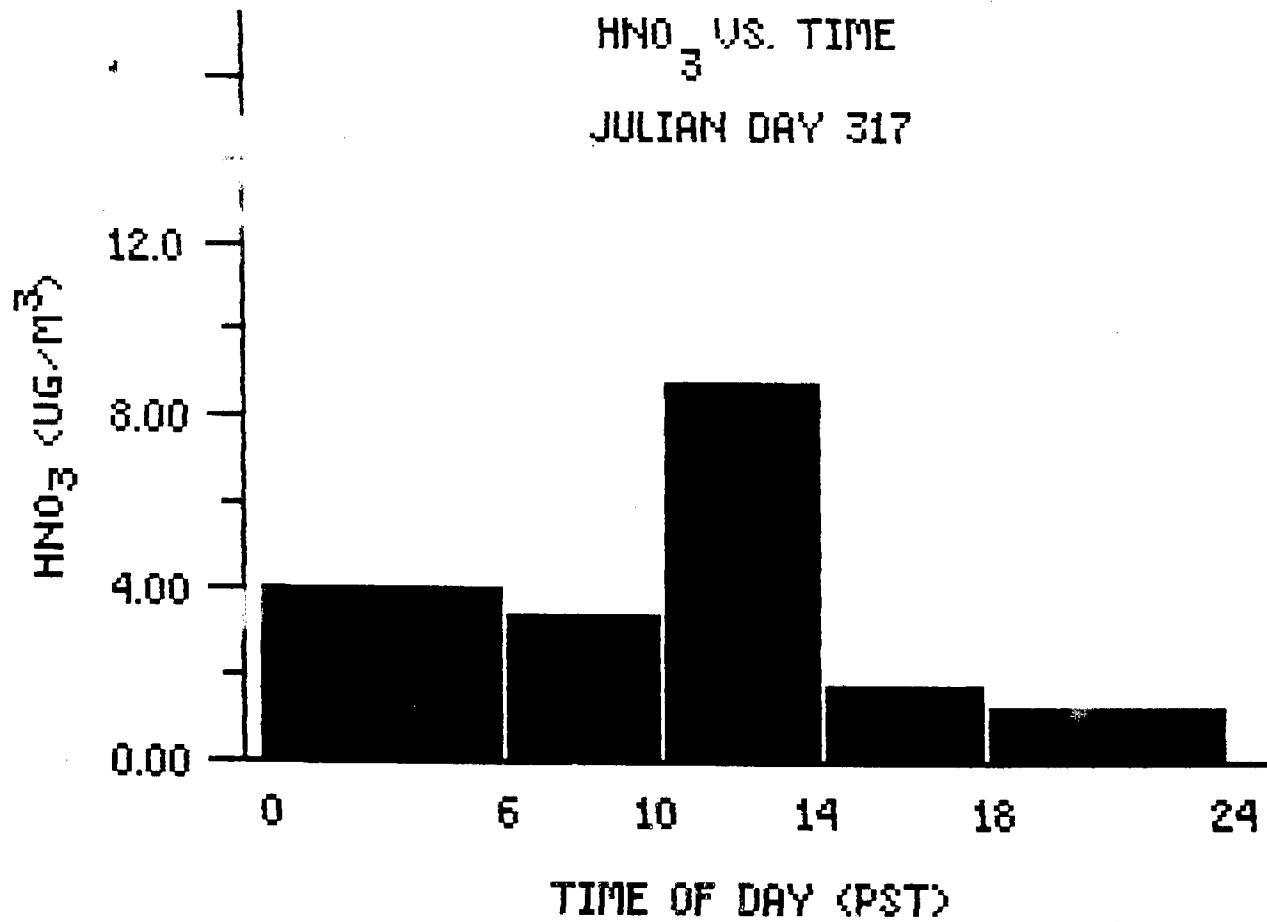
HNO$_3$ VS. TIME

JULIAN DAY 315

Figure 15.

HNO$_3$ VS. TIME

JULIAN DAY 316

Figure 16.

HNO$_3$ VS. TIME

JULIAN DAY 317

Figure 17.

HNO₃ VS. TIME
JULIAN DAY 337

Figure 18.

HNO₃ VS. TIME

JULIAN DAY 344

Figure 19.

HNO₃ VS. TIME

JULIAN
DAY 345

Figure 20

HN03 AGAINST NH3 CONCENTRATIONS

HN03 (UG/M3)

NH3 (UG/M3)

Figure 21.

HC1 VS. TIME
JULIAN DAY 337
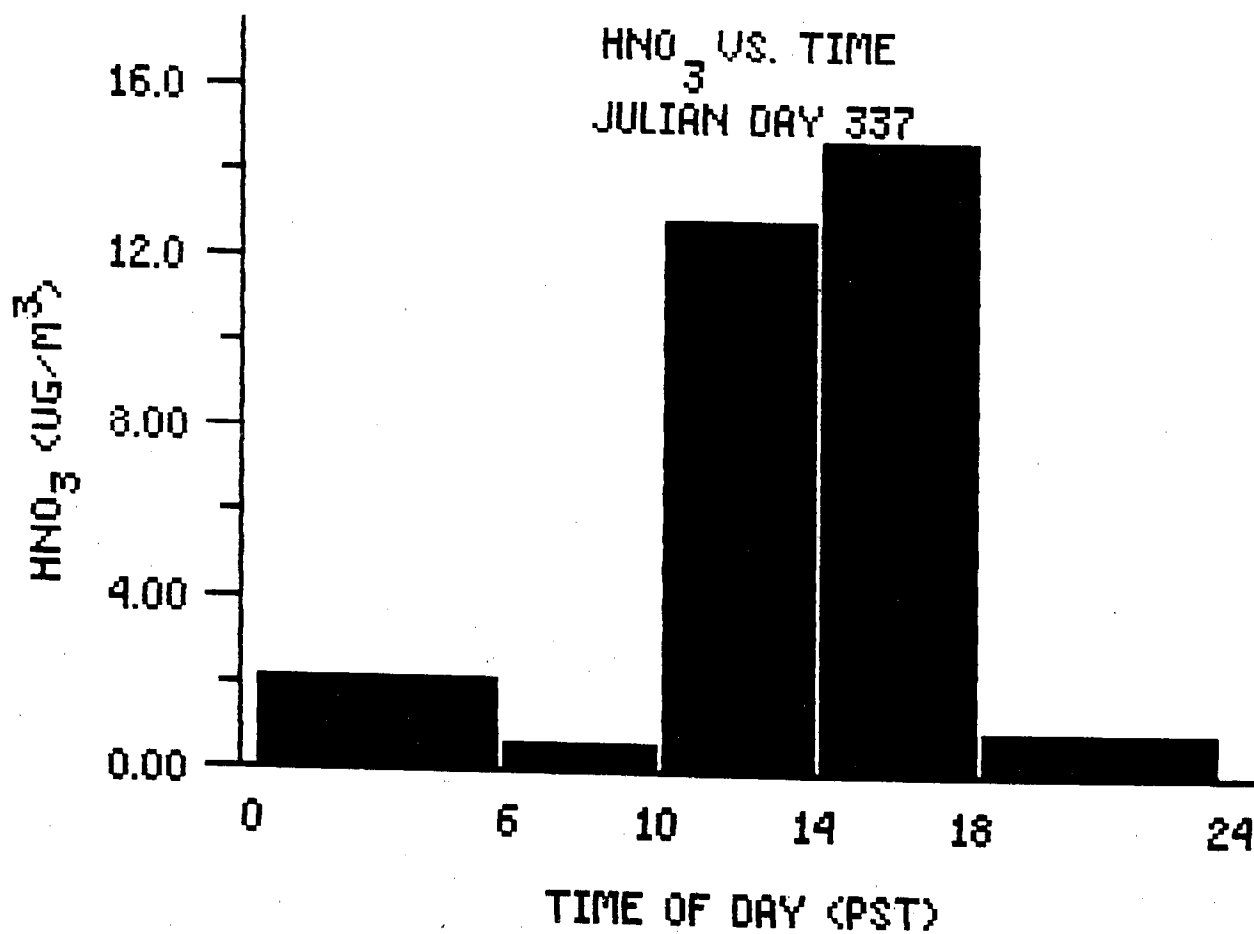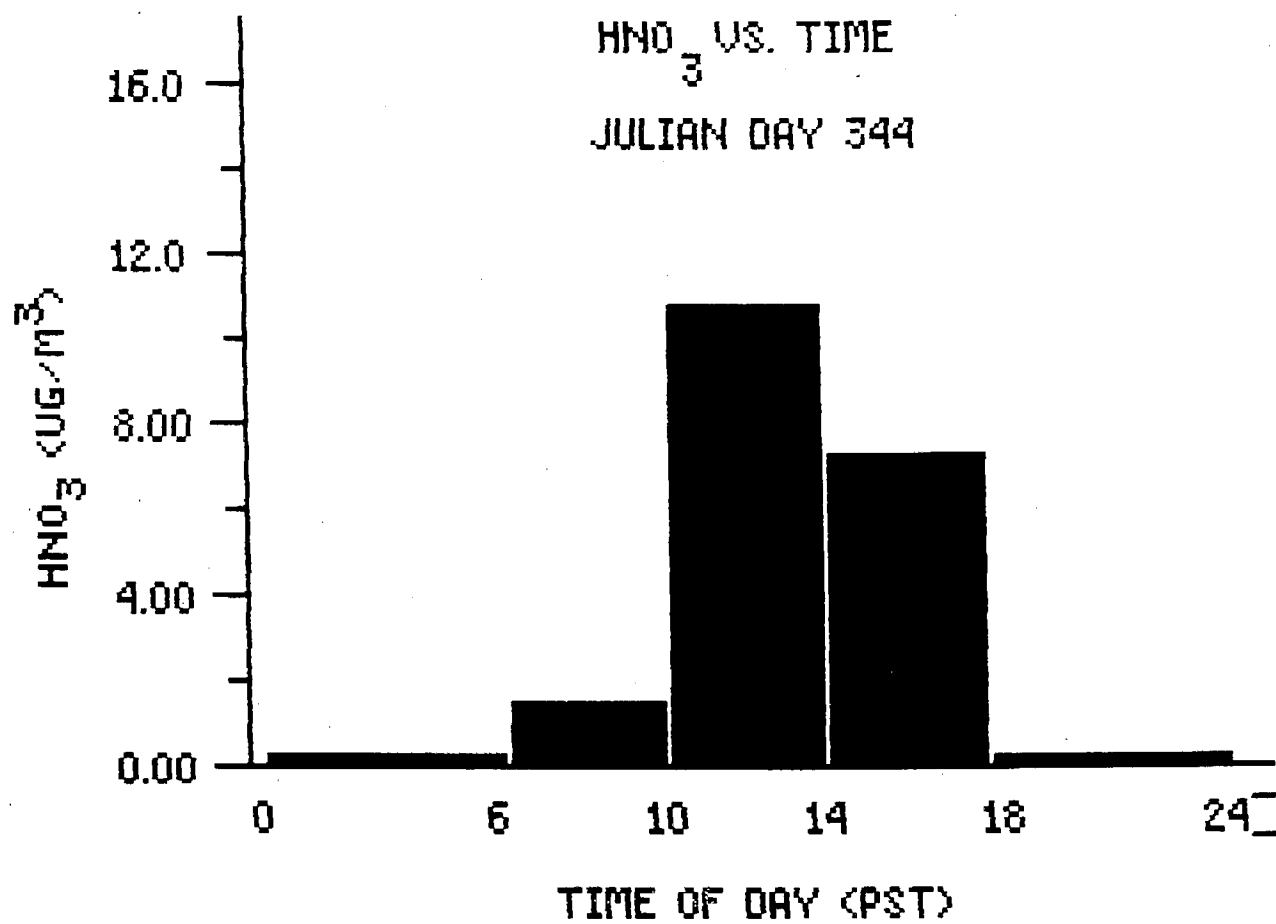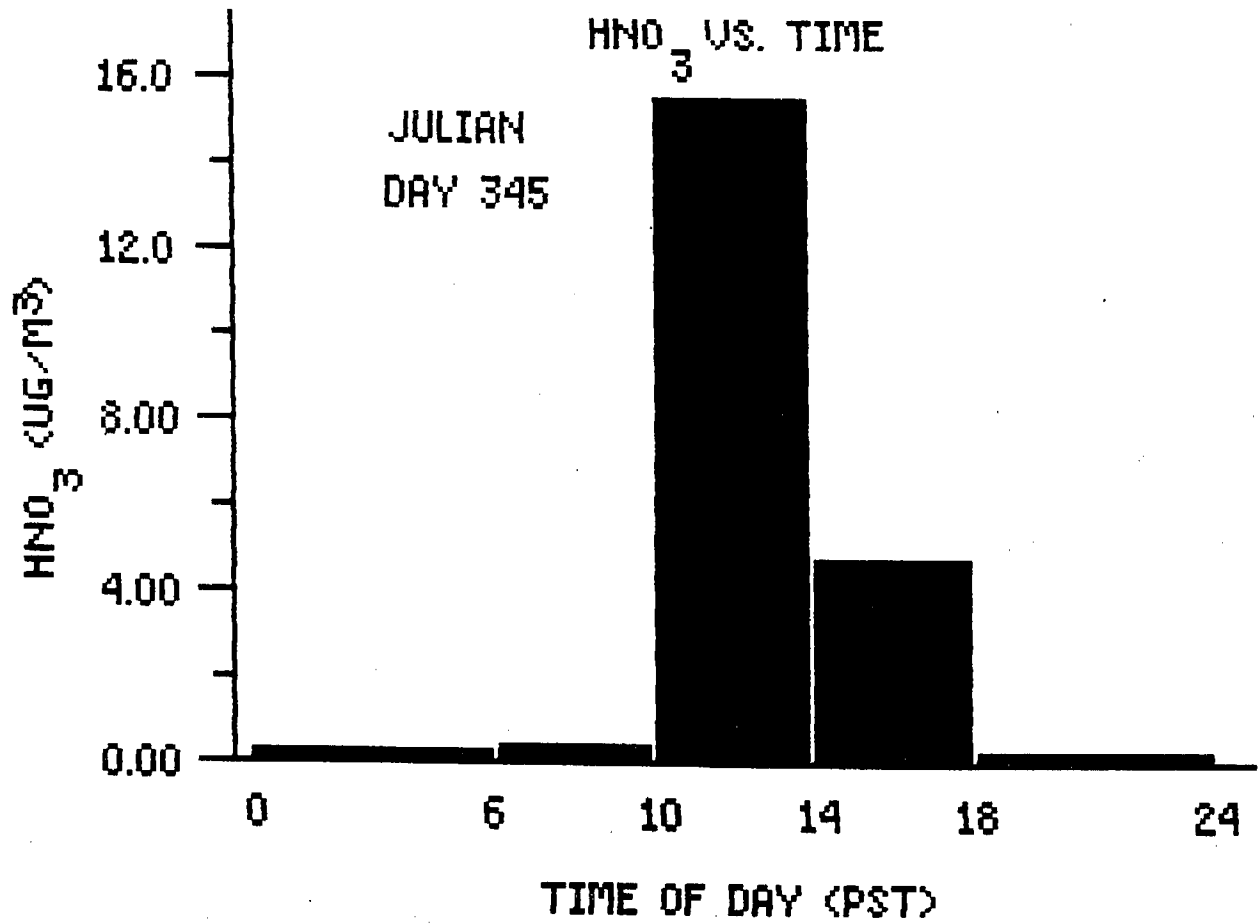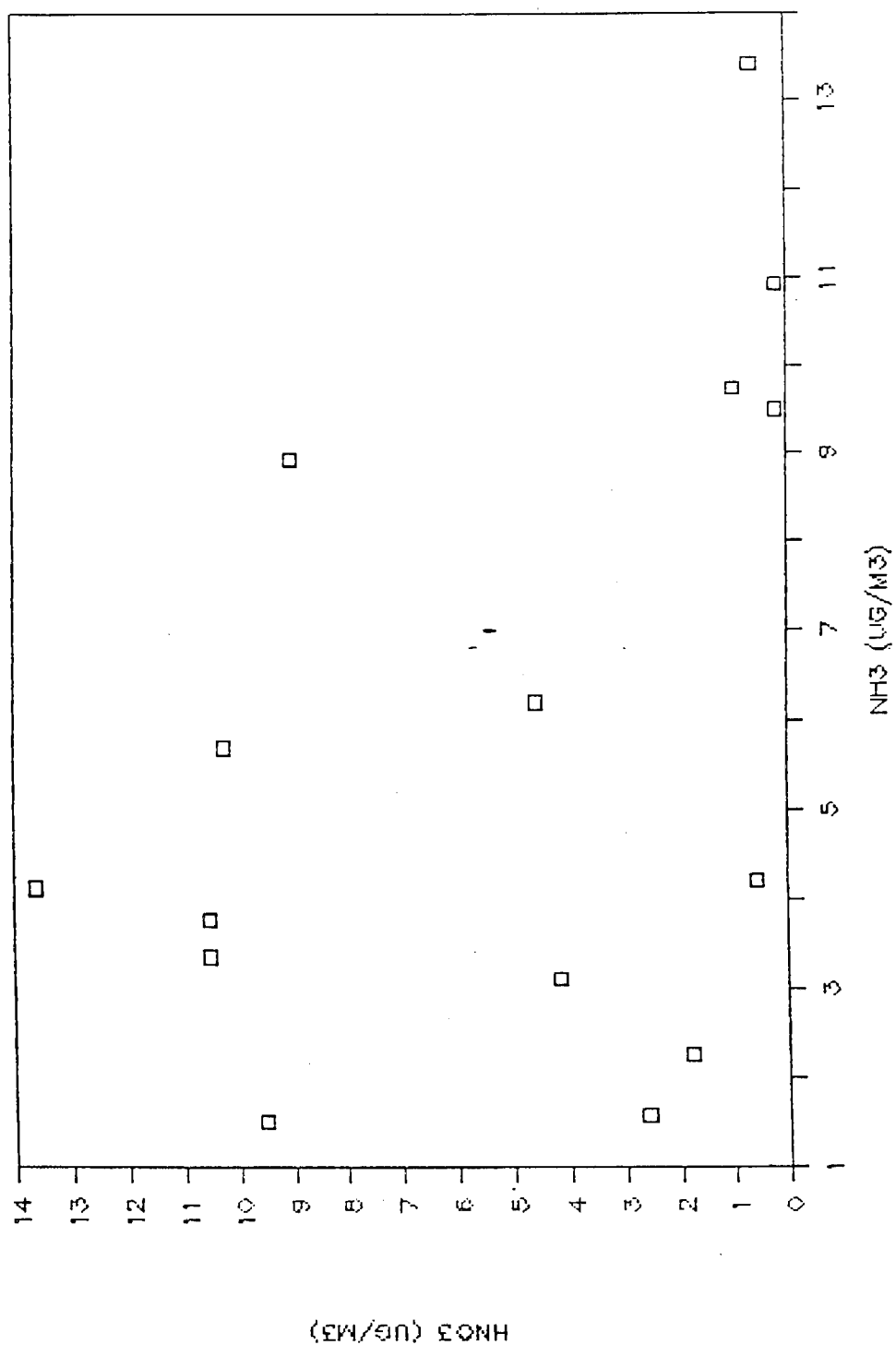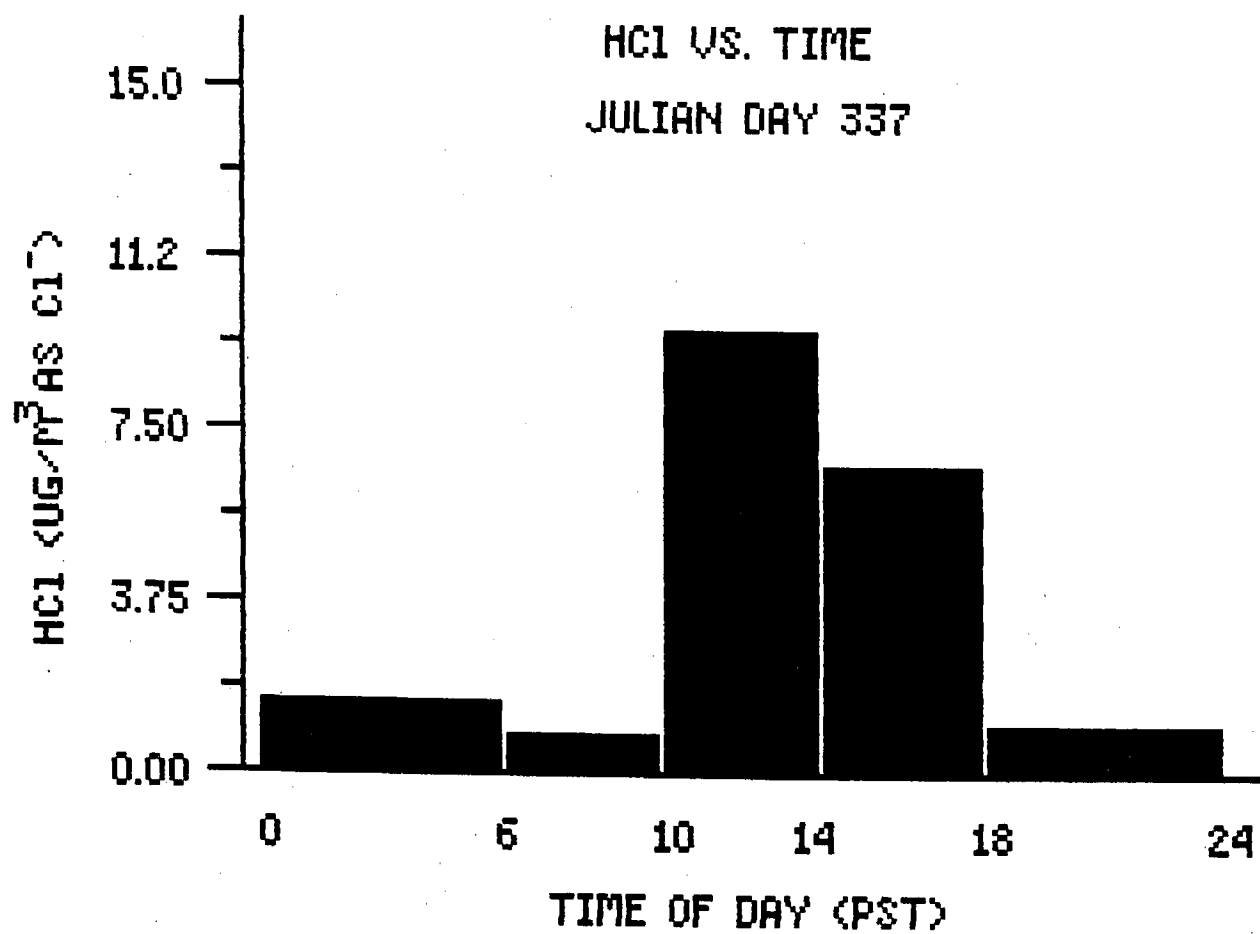
$\mu g/m^3$ (as Cl^-) was found. In all cases, however, daytime maximum were observed.

C. Ammonia Concentrations at Long Beach

Ammonia results obtained with tandem annular denuders are listed in Table 8. On average, 97% of the NH_3 was recovered, as NH_4^+, from the front annular denuder, indicating very high collection efficiency. Appendix D is a listing of NH_3 results, including standard errors, for inclusion in the SCAQS data base. The standard deviations are based on the analytical precision observed with atmospheric samples, with allowance for the measured concentration range. Concentrations for the first three sampling days were highest during the period midnight to 0600. During the December sampling periods, highest concentrations were seen during the 0600-1000 period. Levels up to 11 $\mu g/m^3$, as NH_4^+ (15 ppb) were observed with a mean concentration of 4.9 $\mu g/m^3$ (6.7 ppb).

Long Beach ammonia concentrations obtained in the present study are compared to those using the SCAQS sampler, with analyses by EMSI, in Figure 22. The correlation between data sets was only fair (r = 0.84), with the SCAQS sampler averaging about 30% lower than the annular denuder NH_3 values. These findings are especially notable when contrasted with the comparison of analytical methods (Figure 7); the SCAQS sampler results were obtained with an automated, colorimetric method which showed results averaging 40% higher than those by the SIE used with the annular denuder samplers. Because of sample aging, the 40% difference probably represented a lower limit to the actual difference. Thus differences in analytical methods do not explain the differences in sampler results. These differences are, however, consistent with a substantially greater degree of loss of NH_3 within the SCAQS sampler plumbing relative to such losses to the small, Teflon-coated glass cyclone ahead of the annular denuder.

The delay in analysis of the split solution samples weakens somewhat the conclusions from this comparison. Accordingly, additional side-by-side comparisons of this type should be incorporated into future applications of the SCAQS sampler, preferably with analysis of NH_4^+ from both samplers using the same analytical method.

D. Nitrogen Oxides at Long Beach by a Chemiluminescent NO_x Analyzer

Table 9 lists hourly average concentrations of NO, NO_2, NO_2^+, NO_y, O_3, temperature and relative humidity, where NO_2^+ is the measured hourly average NO_2 concentration without correction, "NO_2" is the hourly average NO_2 sampling through a carbonate-glycerol coated denuder, and $NO_y = NO_2^+ - NO_2$. Also shown are daily mean and overall mean concentrations. Because of a malfunction in the hygrometer, relative humidity and temperature data were obtained only on Julian days 337, 344 and 345. Hourly NO_y concentrations ranged from -15 to 25 ppb, 17% of calculated values being negative. An outlier, -65 ppb NO_y, occurred during a period of rapidly changing NO_2 concentrations, for which the difference technique, as described previously, would be inaccurate. Similarly, NO_y values

Table 8. Ammonia Results at Long Beach

ID	STARTDATE JULIAN	START TIME	FT NH3 UG/M3*	RR NH3 UG/M3*
S011	11/11/87	0000	13.44	0.54
S012		0600	9.49	0.30
S013	(315)	1000	8.93	<.11
S014		1400	5.70	<.11
S015		1800	9.73	<.08
S021	11/12/87	0000	10.80	0.36
S022		0600	4.21	<.11
S023	(316)	1000	4.13	<.11
S024		1400	3.78	<.11
S025		1800	3.37	0.23
S031	11/13/87	0000	6.19	0.35
S032		0600	3.12	0.16
S033	(317)	1000	1.51	<.11
S034		1400	1.59	<.11
S035		1800	2.27	0.10
S041	12/3/87	0000	1.79	0.12
S042		0600	6.15	0.18
S043	(337)	1000	1.64	0.12
S044		1400	0.45	0.15
S045		1800	2.49	<.11
S051	12/10/87	0000	5.56	0.08
S052		0600	14.96	<.11
S053	(344)	1000	6.27	<.11
S054		1400	4.56	<.11
S055		1800	6.76	0.10
S061	12/11/87	0000	2.28	<.08
S062		0600	6.39	<.11
S063	(345)	1000	2.98	<.11
S064		1400	2.72	<.11
S065		1800	7.26	<.08

*Measured as NH4+

Figure 22.

SCAQS SAMPLER VS. ANNULAR DENUDER NH3

LONG BEACH

$Y = 0.48 + 0.69X$
$r = 0.84$
$n = 30$

RATIO OF MEANS, SCAQS SAMPLER/ANNULAR DENUDER = 0.78

AIHL ANNULAR DENUDER NH3 (UG/M3 AS NH4)

SCAQS SAMPLER NH3 (UG/M3 AS NH4)
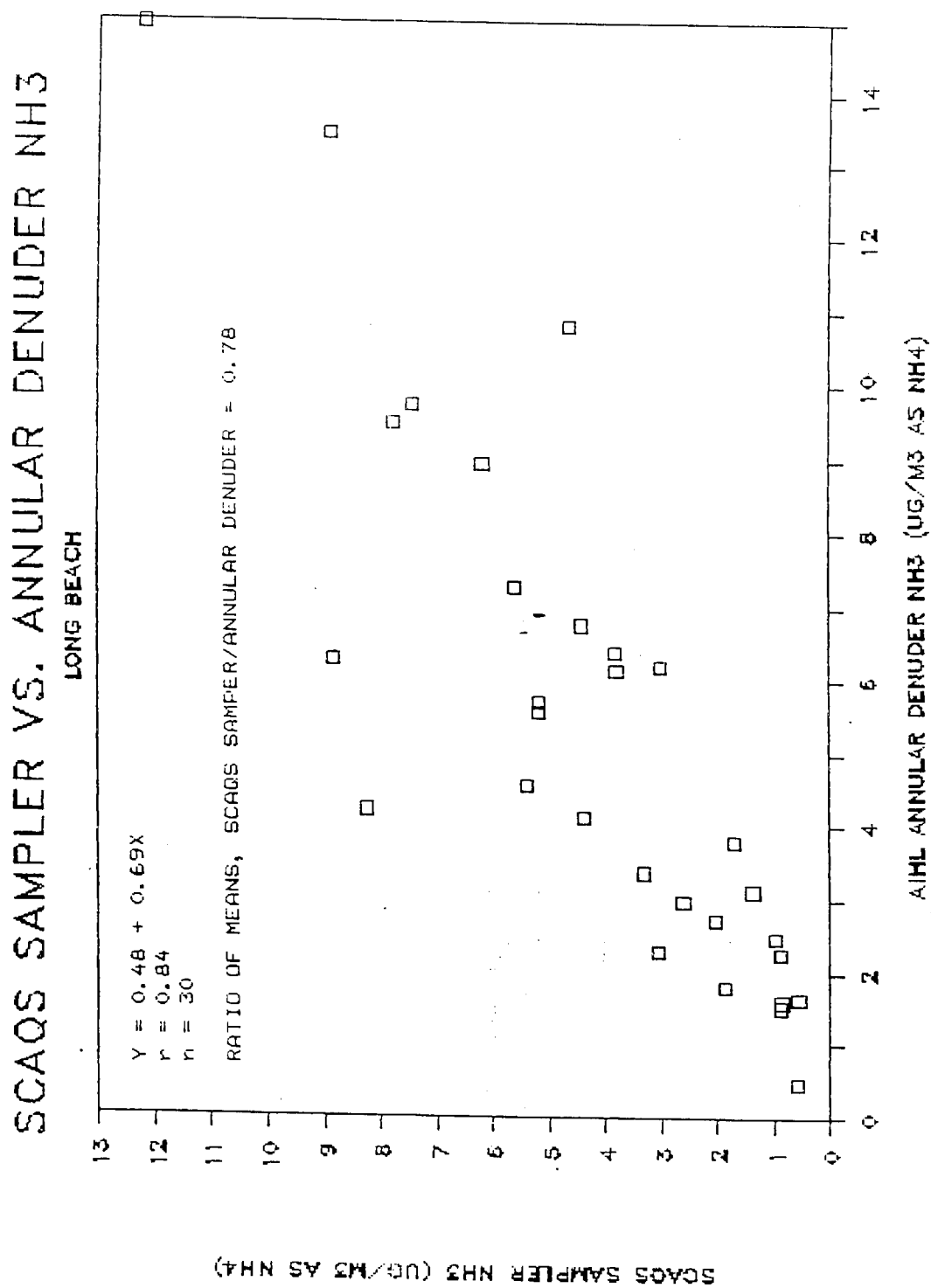
Table 9. NO, NO₂, O₃, T and R.H. Results at Long Beach

JULIAN DAY	TIME (PST)	NO (PPB)	NO2 (PPB)	NO2+ (PPB)	NOY (PPB)	O3 (PPB)	TEMP (oC)	R.H. (%)
315	0100	302.99	22.29	27.53	5.23	10.16		
	0200	173.17	18.42	23.49	5.07	7.84		
	0300	110.30	17.65	20.58	2.93	6.67		
	0400	81.35	17.93	20.32	2.39	6.46		
	0500	86.03	16.75	18.88	2.13	6.53		
	0600	76.14	15.61	17.45	1.84	6.31		
	0700	102.49	16.82	18.32	1.50	4.21		
	0800	142.39	22.98	22.96	-0.02	7.47		
	0900	150.24	47.41	42.99	-4.43	8.27		
	1000	66.08	47.58	61.62	14.04	8.75		
	1100	8.43	34.70	40.22	5.52	14.98		
	1200	<5	39.92	37.12	-2.81	23.38		
	1300	<5	36.29	40.08	3.79	35.93		
	1400	<5	25.59	25.95	0.36	46.55		
	1500	<5	39.64	24.73	-14.91	49.77		
	1600	<5	86.72	85.87	-0.86	31.01		
	1700	11.94	69.59	77.85	8.27	11.61		
	1800	7.75	55.94	57.56	1.62	10.53		
	1900	16.18	51.61	56.17	4.56	10.25		
	2000	12.20	49.65	49.68	0.03	10.78		
	2100	62.17	49.12	52.10	2.98	10.33		
	2200	255.01	34.04	40.99	6.95	11.76		
	2300	236.59	33.91	38.17	4.26	11.38		
	2400	258.06	25.60	33.86	8.27	11.85		
DAILY MEAN:		89.98	36.49	38.94	2.45	15.12		
316	0100	372.93	26.39	32.48	6.08	13.31		
	0200	361.48	28.11	32.74	4.63	12.71		
	0300	345.84	29.07	33.45	4.38	12.56		
	0400	333.33	26.22	35.88	9.66	12.27		
	0500	327.86	23.09	30.19	7.10	12.17		
	0600	337.17	22.20	26.74	4.55	12.09		
	0700	392.73	24.52	28.39	3.87	13.52		
	0800	386.00	37.84	37.53	-0.31	14.44		
	0900	199.86	58.38	53.05	-5.33	12.33		
	1000	77.24	74.81	80.75	5.93	12.56		
	1100	19.32	85.23	79.54	-5.69	17.59		
	1200	15.31	88.71	91.56	2.85	21.14		
	1300	<5	70.51	68.92	-1.59	33.03		
	1400	<5	84.17	92.27	8.10	53.79		
	1500	<5	58.50	61.61	3.11	58.86		
	1600	<5	53.96	49.84	-4.12	43.45		
	1700	<5	98.55	90.79	-7.76	18.00		
	1800	20.84	72.91	85.34	12.44	11.40		
	1900	27.59	47.14	55.27	8.13	8.99		
	2000	37.05	39.02	43.22	4.20	8.41		
	2100	62.90	32.69	37.51	4.82	8.64		
	2200	122.06	23.38	29.75	6.37	9.68		
	2300	160.35	21.76	23.14	1.38	9.94		
	2400	119.10	26.48	30.82	4.34	9.62		
DAILY MEAN:		154.96	48.07	49.58	1.51	18.35		

Table 9.   NO, NO₂, O₃, T and R.H. Results at Long Beach, continued

JULIAN DAY	TIME (PST)	NO (PPB)	NO2 (PPB)	NO2+ (PPB)	NOY (PPB)	O3 (PPB)	TEMP (oC)	R.H. (%)
317	0100	155.69	27.97	34.00	6.03	10.43		
	0200	73.97	33.56	38.04	4.48	8.65		
	0300	36.14	33.82	38.45	4.63	8.10		
	0400	55.26	29.77	35.54	5.77	8.60		
	0500	24.56	34.01	39.46	5.45	8.09		
	0600	29.57	26.33	32.29	5.96	9.16		
	0700	5.76	23.02	27.21	4.19	9.85		
	0800	11.45	24.79	26.77	1.98	11.30		
	0900	12.83	31.06	32.36	1.30	11.14		
	1000	<5	24.01	31.56	7.55	16.62		
	1100	<5	12.84	14.78	1.94	26.72		
	1200	<5	16.35	15.79	-0.56	27.56		
	1300	<5	18.29	18.65	0.36	29.58		
	1400	<5	13.20	14.53	1.34	31.91		
	1500	<5	10.44	9.02	-1.42	30.89		
	1600	<5	8.97	9.47	0.50	29.10		
	1700	<5	12.51	13.45	0.94	24.51		
	1800	<5	20.06	20.65	0.60	21.90		
	1900	<5	23.79	24.22	0.43	19.64		
	2000	<5	10.93	17.43	6.50	24.82		
	2100	<5	11.08	9.06	-2.03	27.06		
	2200	<5	7.72	7.80	0.07	25.70		
	2300	<5	10.36	12.32	1.97	15.21		
	2400	<5	5.05	10.35	5.30	11.86		
DAILY MEAN:		16.21	18.80	21.33	2.53	18.68		
318	0100	<5	<5	<5	--	17.98		
	0200	<5	<5	<5	--	18.52		
	0300	<5	7.08	6.73	-0.35	14.86		
	0400	<5	6.95	8.29	1.34	12.76		
	0500	<5	10.34	10.62	0.28	11.07		
	0600	11.34	12.08	14.13	2.05	10.07		
	0700	7.33	13.98	15.42	1.45	9.67		
	0800							
	0900							
	1000							
	1100							
	1200							
	1300							
	1400							
	1500							
	1600							
	1700							
	1800							
	1900							
	2000							
	2100							
	2200							
	2300							
	2400							

Table 9. NO, NO$_2$, O$_3$, T and R.H. Results at Long Beach, continued

JULIAN DAY	TIME (PST)	NO (PPB)	NO2 (PPB)	NO2+ (PPB)	NOY (PPB)	O3 (PPB)	TEMP (oC)	R.H. (%)
337	0100	286.38	20.37	24.42	4.05	26.05	9.13	68.76
	0200	297.68	15.58	31.04	15.45	24.33	11.77	78.49
	0300	334.58	17.45	27.84	10.39	21.50	12.26	81.91
	0400	337.45	25.90	34.66	8.76	20.64	12.33	83.72
	0500	345.72	32.57	44.13	11.56	21.66	12.54	84.59
	0600	361.47	24.39	36.25	11.86	20.63	12.50	87.16
	0700	418.74	32.79	46.32	13.53	22.53	12.29	85.78
	0800	518.42	46.06	53.03	6.98	24.62	12.36	85.39
	0900	485.02	83.36	91.45	8.09	26.29	12.18	79.84
	1000	146.58	41.23	58.40	17.17	23.82	11.69	70.76
	1100	88.80	120.98	56.38	-64.60	27.49	10.94	61.30
	1200	82.17	169.32	182.80	13.48	32.16	10.63	55.04
	1300	20.73	133.74	131.72	-2.03	37.82	10.13	51.04
	1400	19.66	143.31	142.89	-0.42	43.85	10.83	51.49
	1500	10.29	108.80	120.74	11.94	58.30	11.08	54.76
	1600	10.38	99.94	105.44	5.51	50.79	11.65	59.52
	1700	8.82	107.25	122.39	15.14	38.91	12.21	64.50
	1800	11.36	87.75	93.48	5.73	26.04	12.62	65.87
	1900	52.94	73.18	81.49	8.31	16.70	11.82	67.47
	2000	77.89	60.60	73.97	13.37	15.80	12.53	73.86
	2100	96.83	47.61	58.14	10.53	15.37	12.84	74.73
	2200	146.80	38.67	50.05	11.38	17.27	12.50	69.36
	2300	162.29	34.15	45.47	11.33	18.84	12.14	67.15
	2400	206.18	24.67	32.37	7.70	18.37	11.14	69.63
DAILY MEAN:		188.63	66.24	72.70	6.47	27.07		
344	0100	423.83	36.29	46.09	9.80	21.33	11.12	75.75
	0200	411.52	43.93	56.04	12.11	20.13	11.29	76.92
	0300	412.11	42.57	54.80	12.23	18.80	11.45	77.67
	0400	382.44	40.93	49.86	8.94	17.01	11.53	78.21
	0500	395.40	32.38	42.89	10.52	15.56	11.56	81.17
	0600	433.26	32.16	40.01	7.85	15.42	11.62	81.91
	0700	478.36	26.67	37.47	10.80	15.15	11.53	83.05
	0800	430.38	32.56	38.34	5.78	15.00	11.65	80.39
	0900	269.61	56.02	55.35	-0.67	13.75	11.68	71.87
	1000	218.24	90.84	84.96	-5.88	14.68	11.14	62.95
	1100	116.96	126.39	134.15	7.76	17.35	10.80	54.91
	1200	30.26	74.66	86.65	11.98	17.70	10.04	47.50
	1300	18.90	82.58	83.37	0.79	24.43	9.43	41.97
	1400	37.76	156.74	176.31	19.57	26.45	10.88	46.38
	1500	14.13	80.81	104.98	24.17	23.77	10.14	45.45
	1600	14.61	80.78	87.43	6.65	21.78	10.61	50.51
	1700	27.64	58.01	67.05	9.05	11.17	10.72	55.07
	1800	85.85	29.92	39.00	9.07	10.20	11.92	62.21
	1900	156.10	21.40	28.98	7.58	12.66	12.02	64.92
	2000	161.45	22.31	27.99	5.69	12.21	12.32	74.40
	2100	196.49	15.27	24.32	9.05	15.60	12.73	75.34
	2200	248.36	8.72	15.14	6.41	14.04	13.12	78.89
	2300	359.93	2.33	11.46	9.13	14.50	12.17	80.24
	2400	330.54	7.72	10.72	3.00	15.32	11.31	78.16
DAILY MEAN:		235.59	50.08	58.47	8.39	16.83		

Table 9. NO, NO$_2$, O$_3$, T and R.H. Results at Long Beach, continued

JULIAN DAY	TIME (PST)	NO (PPB)	NO2 (PPB)	NO2+ (PPB)	NOY (PPB)	O3 (PPB)	TEMP (oC)	R.H. (%)
345	0100	410.43	31.10	30.71	-0.39	18.52	10.96	76.67
	0200	355.97	27.09	42.34	15.25	16.10	11.44	78.03
	0300	181.77	32.23	36.13	3.90	12.62	11.86	81.25
	0400	195.64	29.73	37.35	7.62	13.40	11.49	79.69
	0500	184.80	27.26	33.26	6.00	12.81	11.21	81.32
	0600	203.96	19.97	22.97	3.00	12.48	10.87	82.33
	0700	266.09	20.21	26.74	6.54	12.51	10.96	81.54
	0800	397.76	24.02	27.03	3.01	15.15	12.14	75.08
	0900	254.27	37.63	43.50	5.86	11.26	13.01	77.92
	1000	87.66	46.82	45.95	-0.87	10.22	13.38	76.99
	1100	58.44	57.12	61.79	4.67	15.18	13.41	74.30
	1200	35.70	59.75	63.27	3.52	16.46	13.45	69.28
	1300	22.79	62.66	63.35	0.69	19.86	13.47	66.33
	1400	22.27	78.05	76.93	-1.12	24.76	13.46	65.54
	1500	17.69	77.26	72.01	-5.25	25.33	13.27	65.69
	1600	49.85	103.61	107.43	3.82	22.04	13.42	68.17
	1700	35.40	95.27	100.81	5.54	23.90	12.65	67.90
	1800	68.99	85.34	93.07	7.73	20.48	12.06	68.63
	1900	107.52	69.60	78.55	8.95	22.88	12.17	74.62
	2000	181.77	49.84	64.26	14.41	20.35	12.06	75.88
	2100	242.68	39.22	51.74	12.52	20.05	12.02	79.09
	2200	311.86	29.36	42.15	12.79	19.08	11.83	78.76
	2300	374.09	31.98	43.46	11.48	19.41	11.66	79.98
	2400	415.15	50.32	59.54	9.21	21.42	11.43	80.95
DAILY MEAN:		166.22	43.91	49.05	5.14	17.76		
346	0100	403.36	53.45	73.98	20.53	21.39	10.66	81.00
	0200	432.31	34.37	59.33	24.96	22.73	9.64	81.22
	0300	481.65	40.20	60.92	20.72	23.67	9.35	81.88
	0400	498.09	39.07	51.34	12.27	23.00	8.77	81.46
	0500	388.28	30.88	45.62	14.74	19.19	7.93	77.31
	0600	342.93	20.06	32.19	12.13	16.49	6.74	72.30
	0700	272.90	14.72	21.89	7.17	13.98	5.50	66.57
	0800	281.67	18.66	23.79	5.14	14.67	5.46	66.40
OVERALL MEANS:		151.76	42.16	47.75	5.59	18.70	11.10	

may have positive error from such a cause. The mean hourly NO_y value (excluding the outlier) was 5.6 ppb (n=158) for all periods listed. This compares to a mean NO_2 value (with denuder) of 42.2 ppb (n=158). Thus, the use of the carbonate-glycerol coated denuder eliminated what we consider to be a 13% positive error in measured NO_2. Appendix E is a listing of NO, NO_2 and NO_y results, for inclusion in the SCAQS data base.

Figure 23 plots NO_y against NO_2 concentration. No correlation is evident, suggesting that partial removal of NO_2 was not the source of the measured NO_y. The diurnal variations in NO_y are shown for each of the six sampling days in Figures 24 to 29. For graphing purposes, negative NO_y values were plotted as zero concentrations. No consistent trend is evident; daily maxima in NO_y are observed both during nighttime and daytime periods.

Elevated NO_y values are expected both during periods of high HNO_3 (i.e. afternoon) and high HONO (i.e. nighttime) concentrations. Accordingly, the correlation between NO_y concentrations (averaged for corresponding periods) and the sum (in ppb) of HNO_3 and HONO was evaluated (Figure 30). A positive correlation is evident (r=0.67) with much scatter. The present results suggest that additional trials of this type should be made, especially at a site more subject to photochemical smog. A dual channel CA should be used to permit continuous measurement of NO_2 and NO_2^+, thereby greatly improving the accuracy of one-hour mean concentrations of NO_2 and NO_y.

E. Correlation Between HONO and NO2

To assess the significance of Equation (3) as a source of HONO, correlations were determined between nighttime concentrations of HONO and NO_2 and between nighttime HONO and $(NO_2)^2$. For a total of 10 data pairs in each regression, the correlation coefficient was approximately zero. Figure 31 illustrates the latter regression. The inclusion of H_2O vapor concentration would not be expected to enhance the correlation since relatively small H_2O concentration changes were involved in the nighttime samples. Thus, no support for this heterogeneous formation mechanism for atmospheric HONO formation is evident.

F. Correlation Between HNO3 and Ozone Concentrations

As shown in Table 9, O_3 maxima were 50-60 ppb on Julian days 315, 316, 337, with maxima of 25-30 on Julian days 317, 344 and 345. Comparing Tables 6 and 9, HNO_3 concentrations usually occurred in the 1000-1400 hr period, earlier in the day than the O_3 maxima, with the highest HNO_3 occurring on a day with low O_3 maximum. This behavior contrasts with that observed at Claremont (8) and Riverside (20). Such behavior suggests that the observed HNO_3 may have been formed on preceding days. Its survival in the atmosphere may have been enhanced by NH_4NO_3 formation with subsequent dissociation in a region containing lower NH_3 levels.

Figure 23.

NOY AGAINST NO2 CONCENTRATION

Figure 24.

NO$_Y$ CONCENTRATION VS. TIME
JULIAN DAY 315

TIME OF DAY (PDT)

Figure 25.

NO$_Y$ CONCENTRATION VS. TIME
JULIAN DAY 316

Figure 26.

NO$_Y$ CONCENTRATION VS. TIME
JULIAN DAY 317

Figure 27.

NO$_Y$ CONCENTRATION VS. TIME
JULIAN DAY 337

Figure 28.

NO_Y CONCENTRATION VS. TIME
JULIAN DAY 344

Figure 29.

NO_Y CONCENTRATION VS. TIME
JULIAN DAY 345

Figure 30.

$$NO_Y \text{ VS. } HNO_3 + HONO$$

LONG BEACH

$$Y = 0.537 + 0.644 \; X$$
$$r = 0.667$$

NO$_Y$ (PPB)

HNO$_3$ + HONO (PPB)
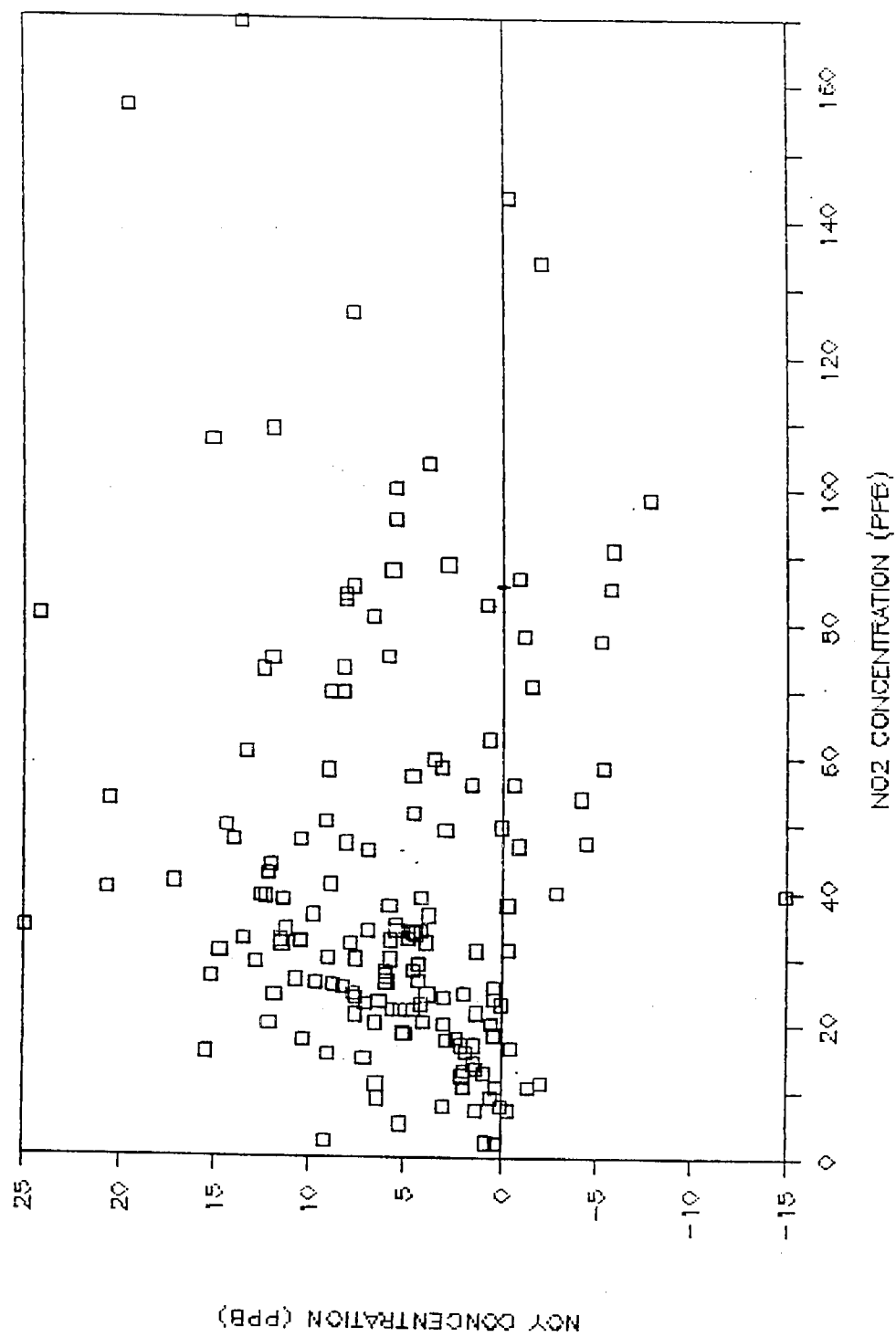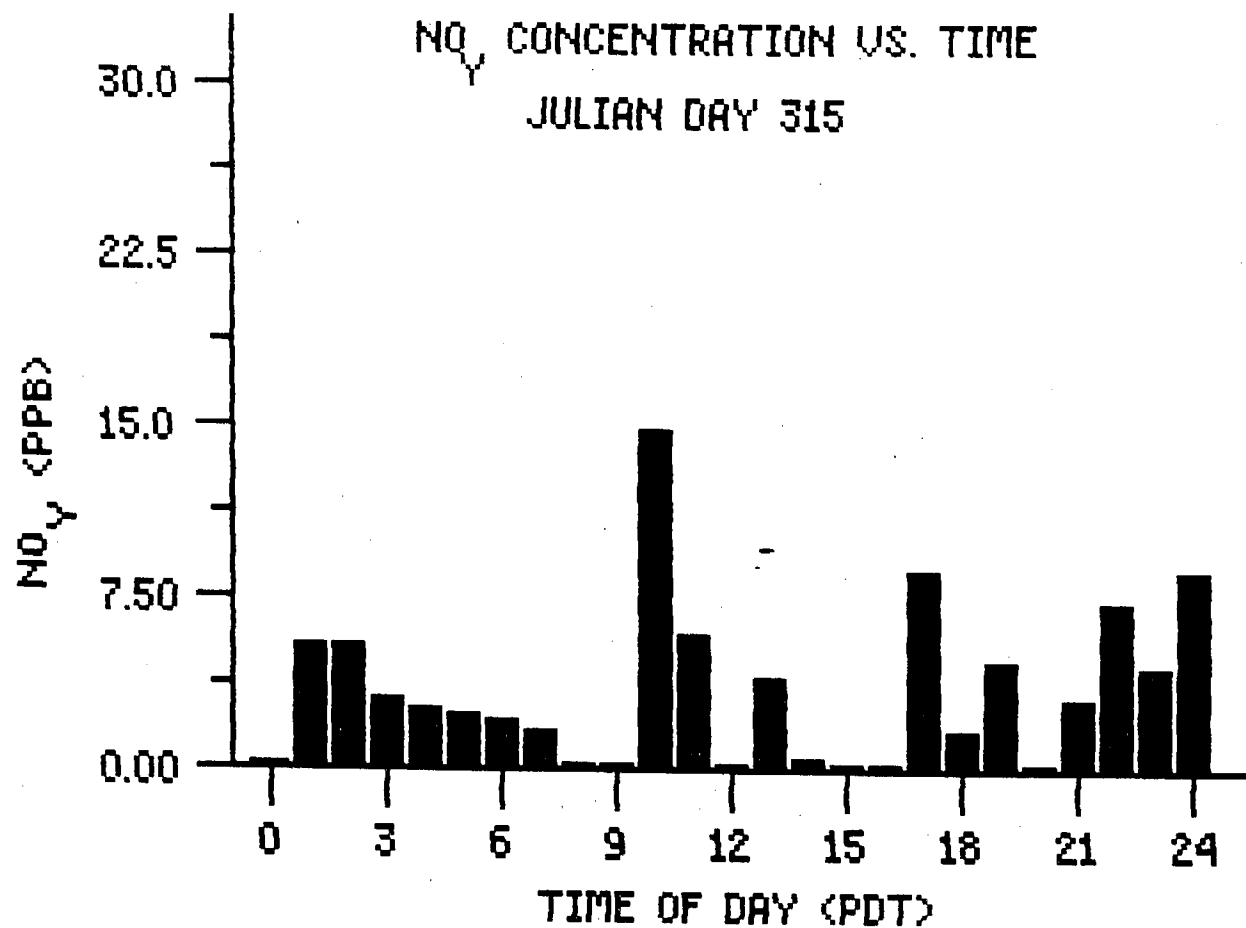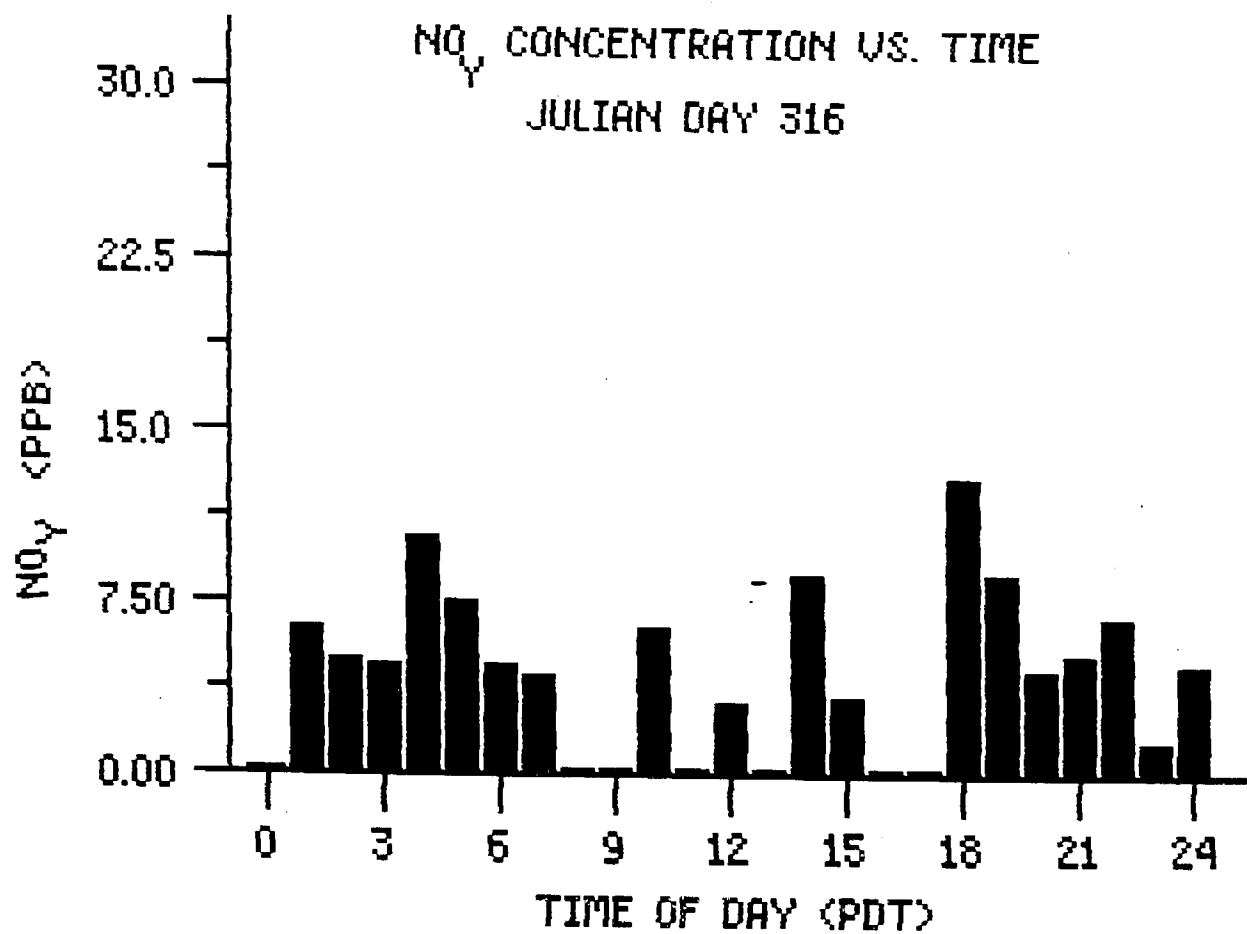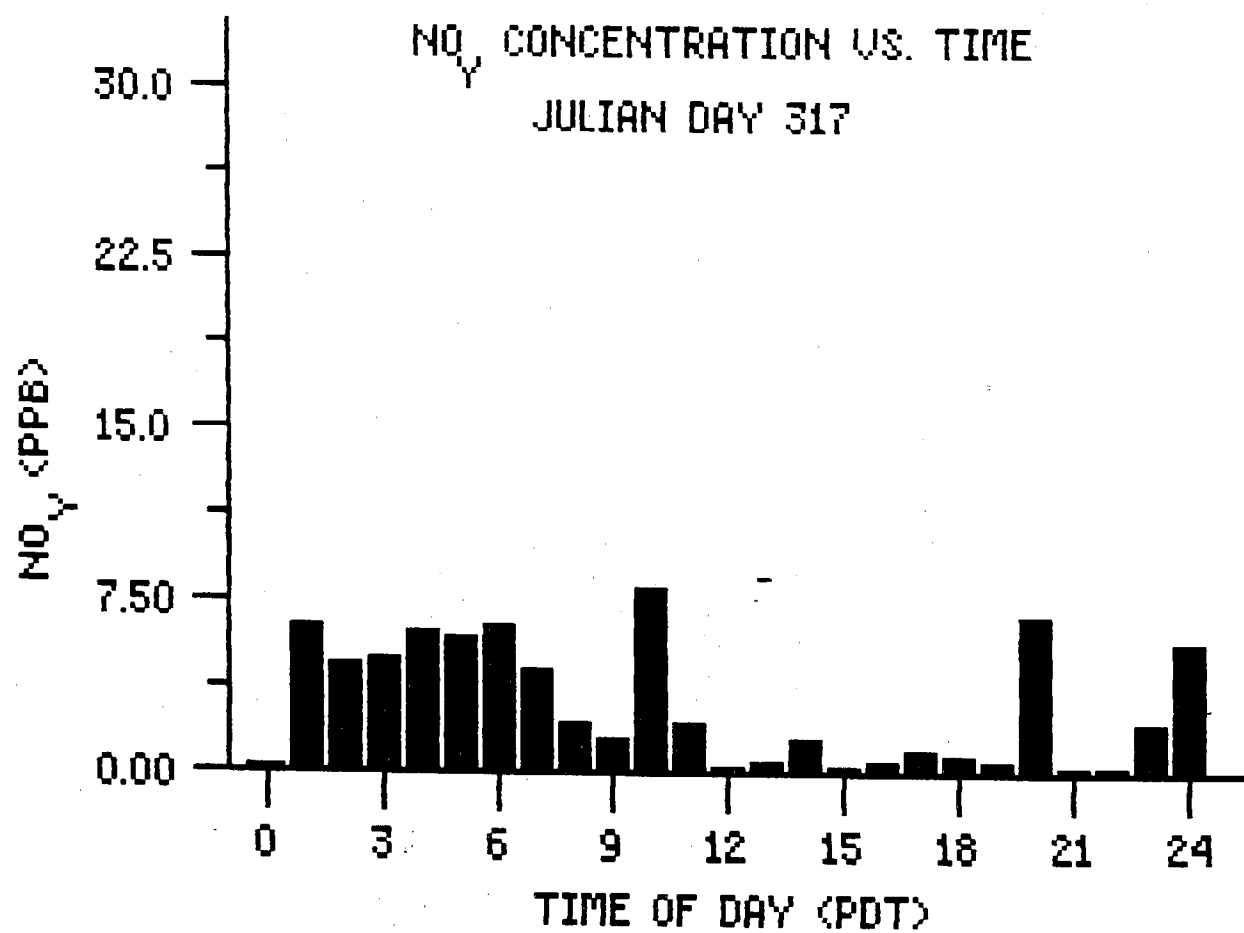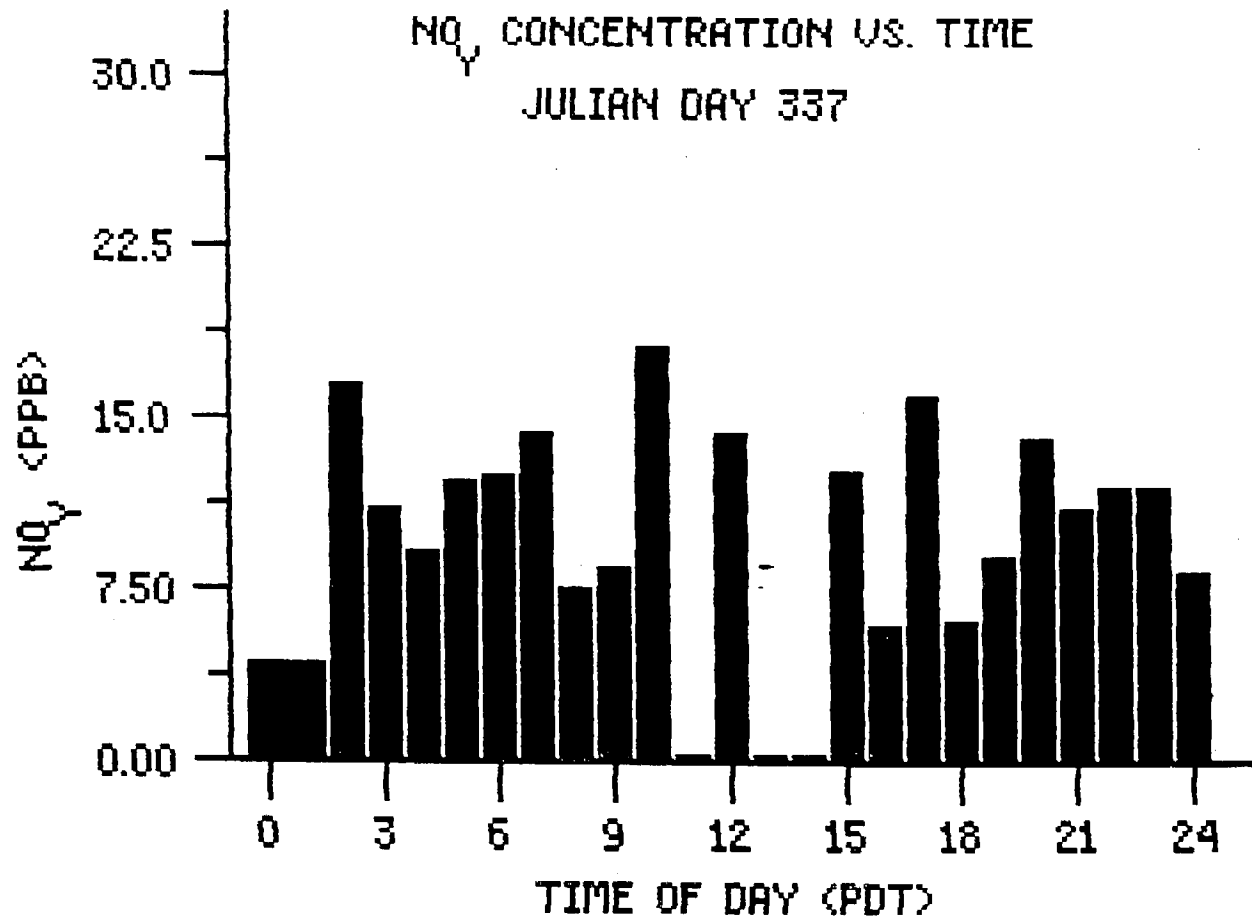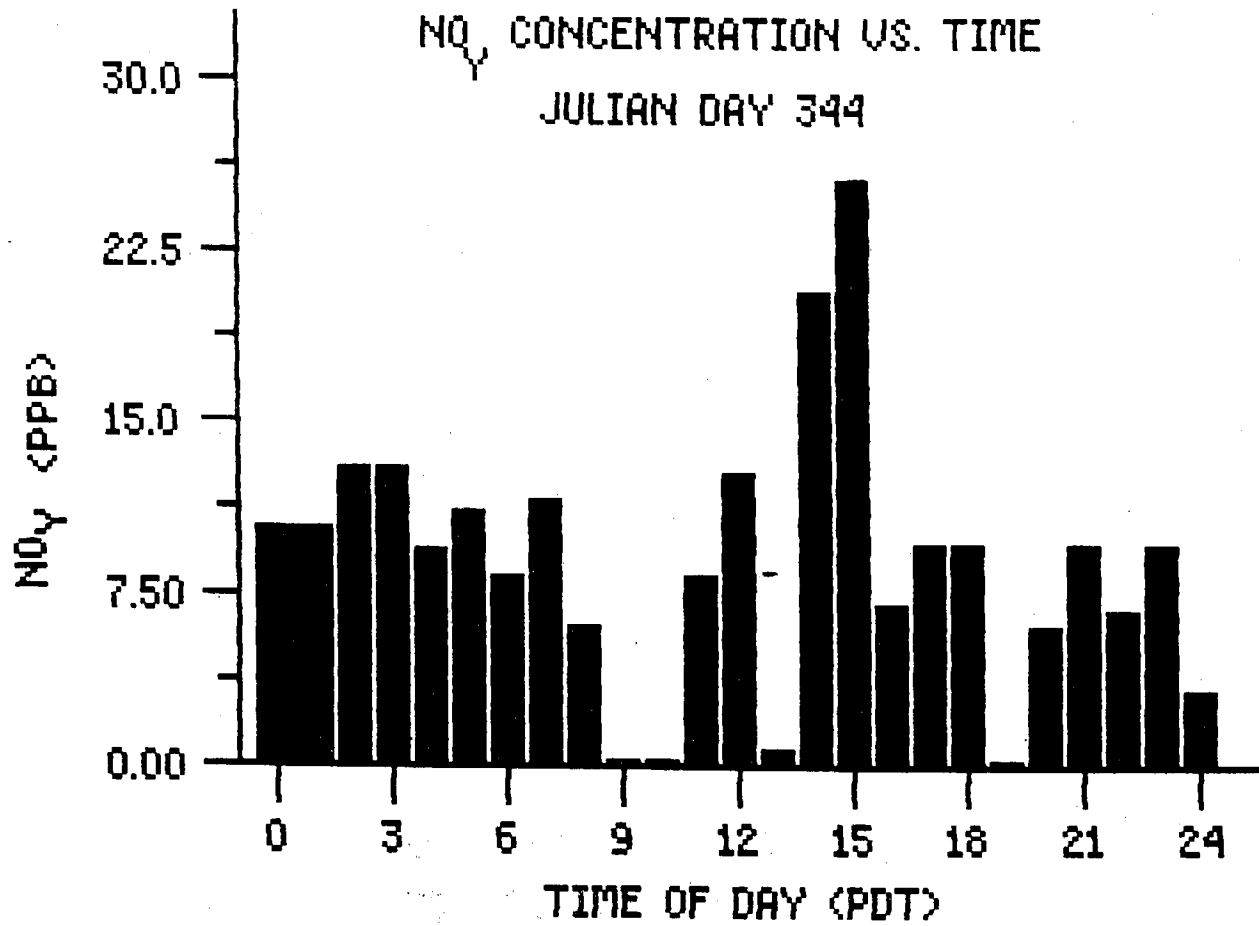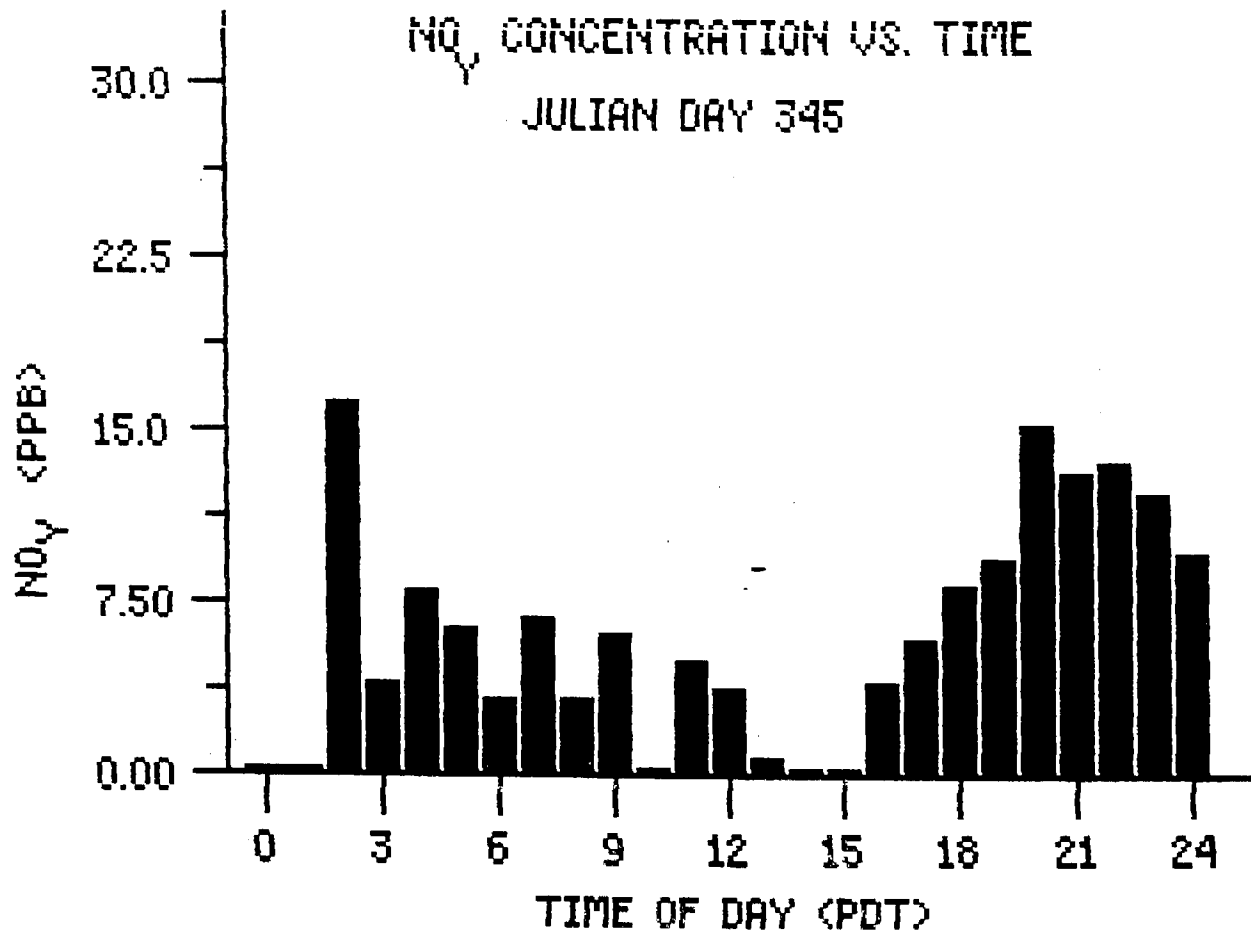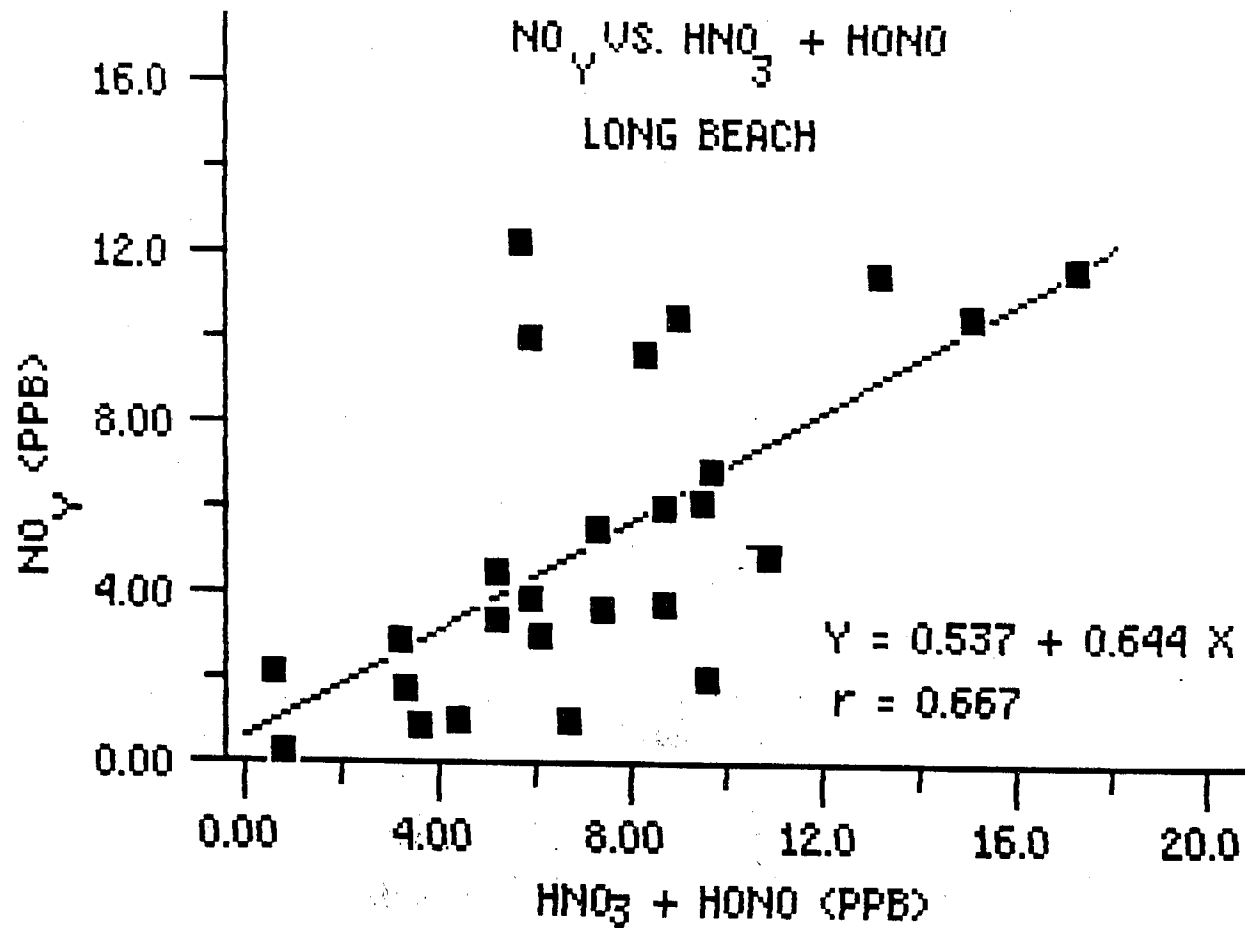
Figure 31.

NIGHTTIME HONO AGAINST NO2*NO2

LONG BEACH

NO2*NO2 (PPB)2
(Thousands)

HONO CONCENTRATION (PPB)
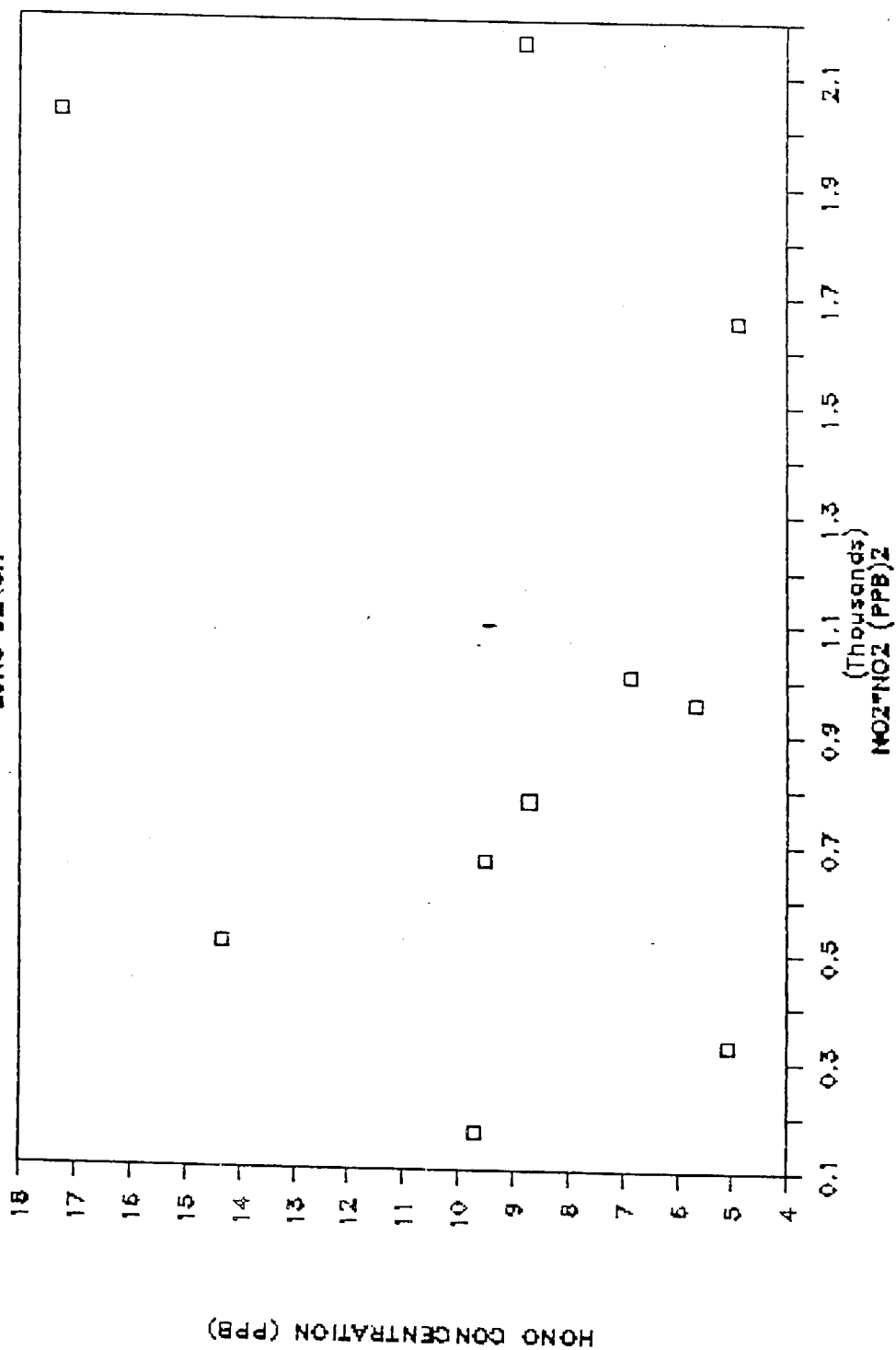
G. <u>HONO as a Predictor of Photochemical Smog Intensity</u>

Since HONO can serve as a source of hydroxy radicals, a key component in photochemical smog formation, a correlation was sought between nighttime (0000-0600 hr) HONO concentrations and smog intensity later on the same day. The maximum hourly O_3 and four-hour maximum HNO_3 are plotted against 0000-0600 hr HONO in <u>Figures 32 and 33</u>. In both cases the correlation is only moderate ($r=0.6-0.7$). Additional evaluations of this type must be made, preferably including a measure of the morning UV flux, before conclusions are warranted.

Figure 32.

MAX. HNO$_3$ VS. NIGHTTIME HONO

Y = 9.3 + 0.39 X

r = 0.70

HNO$_3$ (PPB)

0000-0600 HONO (PPB)

Figure 33.

MAX. O$_3$ VS. NIGHTTIME HONO

Y = 26.7 + 2.1 X

r = 0.63

X-axis: 0000-0600 HONO (PPB)

Y-axis: OZONE (PPB)
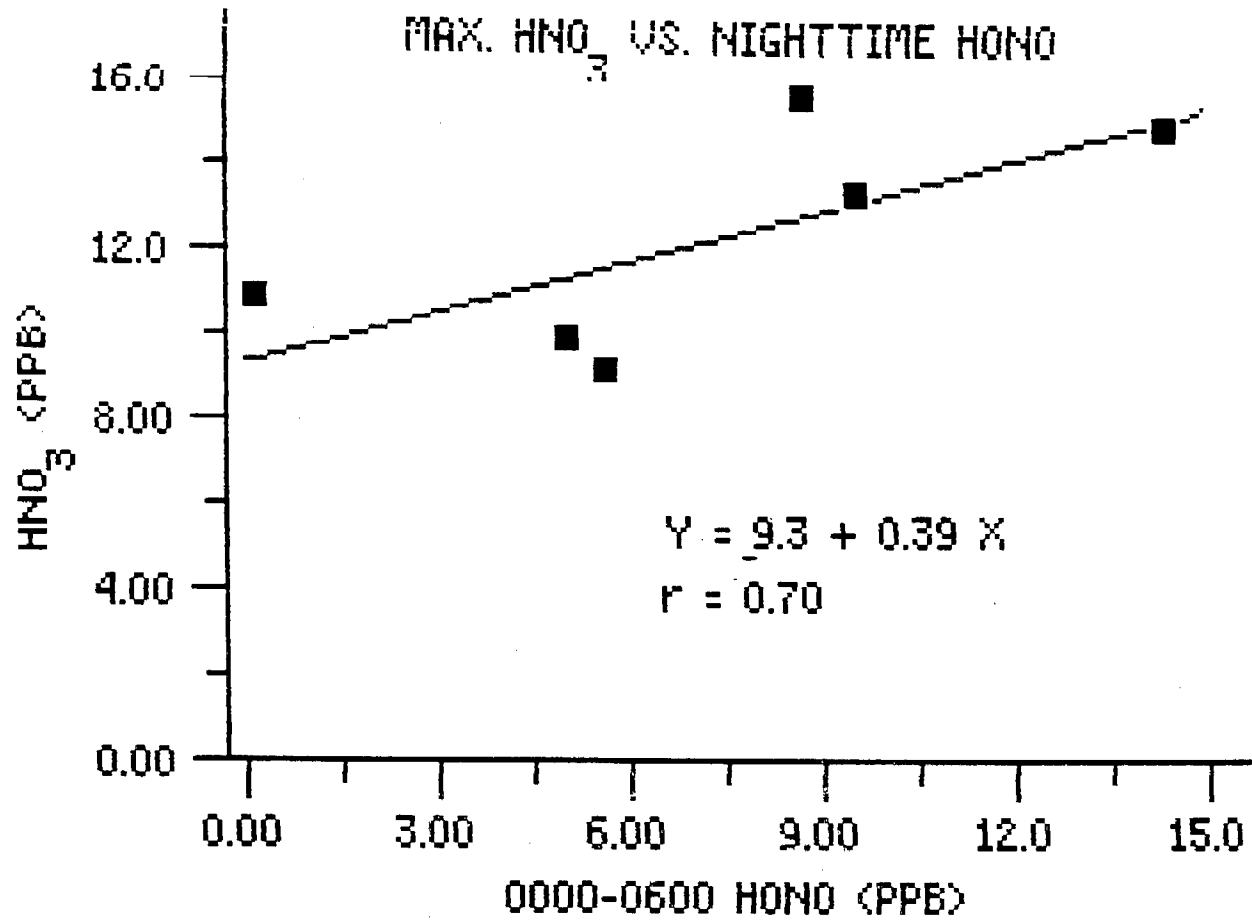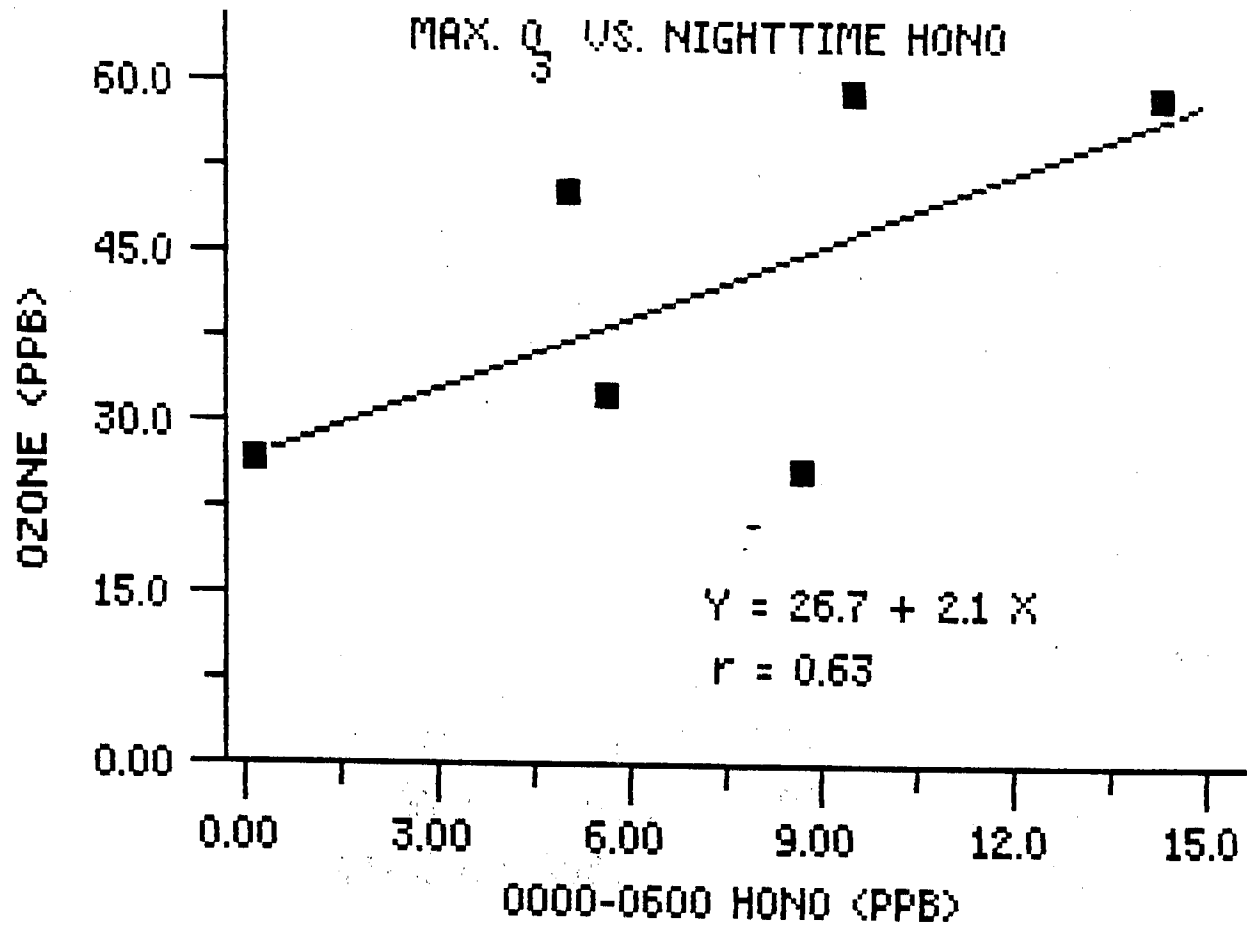
REFERENCES

1. Fontijn, A., Sabadell, J.J. and Ronco, R.J. Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Anal. Chem. $\underline{42}$:575 (1970).

2. Winer, A.M., Peters, J.W., Smith, J.P. and Pitts, J.N., Jr. Responses of Commercial Chemiluminescent $NO-NO_2$ Analyzers to Other Nitrogen-Containing Compounds. Environ. Sci. Technol. $\underline{8}$:1118-1121 (1974).

3. Sickles, J. Research Triangle Institute, Private communication, 1987.

4. Appel, B.R., Wall, S.M., Tokiwa, Y. and Haik, M. Simultaneous Nitric Acid, Particulate Nitrate and Acidity Measurements in Ambient Air. Atmos. Environ. $\underline{14}$:549-554 (1980).

5. Schiff, H.I., Hastre, D.R., MacKay, G.I., Iguchi, T. and Ridley, B.A. Tunable Diode Laser Systems for Measuring Trace Gases in Tropospheric Air. Environ. Sci. Technol. $\underline{17}$:352A-369A (1983).

6. Appel, B.R., Tokiwa, Y., Povard, V. and Kothny, E.L. Determination of Acidity in Ambient Air--Phase II. Final Report to the ARB, Contract A4-074-32 (1987).

7. Sanhueza, E., Plum, C.N. and Pitts, J.N., Jr. Positive Interference of Nitrous Acid in the Determination of Gaseous HNO_3 by the NO_x Chemiluminescence-Nylon Cartridge Method: Applications to the Measurements of PPB Levels of HONO in Air. Atmos. Environ. $\underline{18}$:1029-1031 (1984).

8. Appel, B.R., Tokiwa, Y., Kothny, E.L., Wu, R. and Povard V. Studies of Dry Acid Deposition in the South Coast Air Basin: Intermethod Comparison of Procedures for Nitric Acid and Ammonia. Final Report to the ARB. Contract 4-147-32 (1986).

9. Possanzini, M. Febo, A. and Leberti, A. New Design of a High-Performance Denuder for the Sampling of Atmospheric Pollutants. Atmos. Environ. $\underline{17}$:2605-2610 (1983).

10. Stevens, R.K., Paur, R.J., Allegrini, I., DeSantis, F., Febo, A., Perrino, C., Possanzini, M., Cox, K.W., Estes, E.E., Turner, A.R. and Sickles, II, J.E. Measurement of HNO_3, SO_2, NH_3 and Particulate Nitrate with an Annular Denuder System. Fifth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources. Raleigh, NC, May 1985.

11. Ferm, M. and Sjodin, A. A Sodium Carbonate Denuder for Determination of Nitrous Acid in the Atmosphere. Atmos. Environ. $\underline{19}$:979-983 (1985).

12. Sjodin, A. and Ferm, M. Measurements of Nitrous Acid in an Urban Area. Atmos. Environ. $\underline{19}$:985-992 (1985).

13. Perner, D. and Platt, U. Detection of Nitrous Acid in the Atmosphere by Differential Optical Absorption. Geophys. Res. Let. $\underline{6}$:917-920 (1979).

14. R. Braman, unpublished studies (1986).

15. Pitts, Jr., J.K., Sanhueza, E., Atkinson, R., Carter, W.P.L., Winer, A.M., Harris, G.W. and Plum, C.N. An Investigation of the Dark Formation of Nitrous Acid in Environmental Chambers. Int. J. Chem. Kinetics 16:919 (1984).

16. Atkinson, R., Carter, W.P.L., Pitts, Jr., J.K. and Winer, A.M. Discussion of paper, Measurements of Nitrous Acid in an Urban Area, A. Sjodin and M. Ferm. Atmos. Environ. 20:408-409 (1986).

17. Appel, B.R., Tokiwa, Y. and Haik, M. Sampling of Nitrates in Ambient Air. Atmos. Environ. 15:283-289 (1980).

18. Allegrini, I., DeSantis, F., DiPalo, V. and Liberti, A. Measurement of Particulate and Gaseous Ammonia at a Suburban Area by Means of Diffusion Tubes (Denuders). J. Aerosol Sci. 15:465-471 (1984).

19. Stelson, A.W. and Seinfeld, J.J. Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant. Atmos. Environ. 16:983-992 (1982).

20. Appel, B.R., Tokiwa, Y., Povard, V., Kothny, E.L. and Wesolowski, J.J. Determination of Acidity in Ambient Air. Final Report to the ARB, Contract A1-159-32 (1984).

21. Appel, B.R., Tokiwa, Y., Hoffer, E.M., Kothny, E.L., Haik, M. and Wesolowski, J.J. Evaluation and Development of Procedures for Determination of Sulfuric Acid, Total Particle-Phase Acidity and Nitric Acid in Ambient Air--Phase II. Final Report to the ARB, Contract A8-111-31 (1980).

22. AeroVironment, Design and Testing of the SCAQS Sampler for the Southern California Air Quality Study. AV Report FR-87/649, Monrovia (1987).

23. Appel, B.R., Povard, V. and Kothny, E.L. Loss of Nitric Acid with Inlet Devices for Atmospheric Sampling. Submitted for Publication to Atmospheric Environment (1987).

24. Winer, A.M., Atkinson, R., Arey, J., Biermann, H.W., Tuazon, E.C. and Zielinska, Z. Role of Nitrogen Pollutants in the Formation of Atmospheric Mutagens and Acid Deposition. Final Report to the ARB, Contract No. A4-081-32 (1987).

25. Peake, E. and Legge, A. Evaluation of Methods Used to Collect Air Quality Data at Remote Sites in Alberta, Canada. Presented at the EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants. Research Triangle Park, NC (May 1987).

26. Bolleter, W.T., et al, Anal. Chem. 33:592 (1961).

APPENDIX A

PROCEDURE FOR COATING AND EXTRACTING ANNULAR DENUDERS
FOR HONO, HNO$_3$ AND HCl COLLECTION

COATING

1. Prepare and check for NO$_2^-$ and NO$_3^-$ blank:

    a)   2%w Na$_2$CO$_3$ in H$_2$O

    b)   2%w glycerol in MeOH

2. Just before coating, make sufficient volume of 50:50 v/v of solutions "a" and "b".

3. Denuders, caps and couplers should be washed prior to initial use by rinsing with H$_2$O followed by MeOH. Components not contacted by extraction solution are rewashed before each subsequent use. Drain solvent.

4. Front and rear sections are coated separately. Cap bottom. Add 10 mL 50:50 solution. Cap top. Swirl to bathe uniformly the interior. Drain.

5. Blow purified, dry ambient air through each section until dry, with the section oriented vertically, and flow upward. Air is purified by passage through a carbonate-glycerol impregnated quartz filter followed by a silica gel cartridge and then a glass fiber filter. The exhaust is vented outside.

6. Cap both ends. When ready for sampling, join sections with coupler.

EXTRACTING

1. Following sampling, separate labelled sections and cap.

2. To one tube add 5.00 mL standard IC eluent with a re-pipet. Cap and rotate to wash surface. Drain with small funnel into prelabelled, color-coded 15 mL screw cap polystyrene test tube. Repeat with a second 5 mL aliquot. Note: about 0.3 mL remains in denuder.

APPENDIX B

PROCEDURES FOR COATING AND EXTRACTING ANNULAR DENUDERS FOR AMMONIA COLLECTION

COATING

1. Prepare and check for NH_4^+ blank 1.5%w citric acid, 5.0%v glycerol in methanol.

2. Denuders, caps and couplers should be washed prior to first use with H_2O and MeOH. Components not contacted by extraction solution are rewashed before each subsequent use. Drain solvent.

3. Front and rear sections are coated separately. Cap bottom. Add 10 mL coating solution. Swirl to bathe uniformly the interior. Drain.

4. Blow purified, dry ambient air through each section until dry, with the section oriented vertically and flow upward. Air is purified by passage through a thick quartz filter (Whatman QMB) impregnated with the citric acid-glycerol mixture, and then through silica gel and a glass fiber filter. The exhaust is vented outside.

5. Cap both ends. When ready for sampling, join sections with coupler.

EXTRACTING

1. Following sampling, separate sections A and B and cap.

2. Add 5.0 mL deionized water with a re-pipet. Cap and rotate to wash surface. Drain with small funnel into prelabelled, color-coded 15 mL screw cap polystyrene test tube. Repeat with a second 5 mL aliquot. Note: about 0.3 mL remains in denuder.

LISTING OF HONO, HNO_3 AND HCl RESULTS FOR THE SCAQS DATA BASE

PROGRAM NAME: SCAQS
ORGANIZATION: AIHL(APPEL)
SITE NAME: LONG BEACH
SAMPLER: ANNULAR DENUDER (CARBONATE-GLYCEROL COATED)
ANALYSIS: HONO, HNO3, HCl
 UNITS: HONO,PPB(v) CALCULATED AT 25 oC
                 HNO3,PPB(V) CALCULATED AT 25 oC
                 HCl,PPB(V) CALCULATED AT 25 oC
PRECISION: BASED ON ANALYTICAL PRECISION ONLY

ID	DATE (JULIAN DATE)	START TIME(PST)	END TIME(PST)	HONO PPB	HONO STD ERROR PPB	HNO3 PPB	HNO3 STD ERROR PPB	HCl PPB	HCl STD ERROR PPB
S011	11/11/87	0000	0550	5.09	0.51	0.14	0.01	<0.3	--
S012		0600	0950	2.53	0.25	0.77	0.08	2.10	0.10
S013	(315)	1000	1350	<0.6	--	3.41	0.34	5.14	0.26
S014		1400	1750	1.40	0.14	3.91	0.39	4.17	0.21
S015		1800	2350	4.92	0.49	0.28	0.03	0.59	0.03
S021	11/12/87	0000	0550	9.55	0.96	<0.2	--	<0.3	--
S022		0600	0950	6.03	0.60	<0.3	--	<0.3	--
S023	(316)	1000	1350	1.50	0.15	5.27	0.53	7.42	0.37
S024		1400	1750	0.43	0.04	4.02	0.40	3.55	0.18
S025		1800	2350	6.88	0.69	4.08	0.41	3.01	0.15
S031	11/13/87	0000	0550	5.69	0.57	1.71	0.17	3.48	0.17
S032		0600	0950	4.45	0.45	1.48	0.15	1.49	0.07
S033	(317)	1000	1350	<0.6	--	3.62	0.36	7.38	0.37
S034		1400	1750	<0.6	--	0.84	0.08	2.66	0.13
S035		1800	2350	<0.6	--	0.59	0.06	1.52	0.08
S041	12/3/87	0000	0550	14.34	1.43	0.85	0.08	1.06	0.05
S042		0600	0950	12.96	1.30	0.26	0.03	0.59	0.09
S043	(337)	1000	1350	3.62	0.36	5.16	0.52	6.71	0.34
S044		1400	1750	2.55	0.26	5.88	0.59	4.64	0.23
S045		1800	2350	8.79	0.88	0.23	0.02	0.70	0.04
S051	12/10/87	0000	0550	<0.4	--	<0.2	--	<0.3	--
S052		0600	0950	*	--	0.59	0.06	<0.4	--
S053	(344)	1000	1350	1.72	0.17	4.31	0.43	5.05	0.25
S054		1400	1750	2.90	0.29	2.88	0.29	4.16	0.21
S055		1800	2350	9.71	0.97	<0.2	--	<0.3	--
S061	12/11/87	0000	0550	8.73	0.87	<0.2	--	<0.3	--
S062		0600	0950	7.46	0.75	<0.3	--	<0.4	--
S063	(345)	1000	1350	3.54	0.35	6.21	0.62	7.47	0.37
S064		1400	1750	4.25	0.42	1.88	0.19	2.06	0.10
S065		1800	2350	17.28	1.73	<0.3	--	<0.3	--

*Not determined.

APPENDIX D

LISTING OF NH$_3$ RESULTS FOR THE SCAQS DATA BASE

PROGRAM NAME: SCAQS
ORGANIZATION: AIHL(APPEL)
SITE NAME: LONG BEACH
SAMPLER: ANNULAR DENUDER (CITRIC ACID-GLYCEROL COATED)
ANALYSIS: AMMONIA AS NH4+ (BY SPECIFIC ION ELECTRODE)
UNITS: PPB(V) CALCULATED AT 25 oC
PRECISION: BASED ON ANALYTICAL PRECISION ONLY

ID	DATE (JULIAN DATE)	START TIME(PST)	END TIME(PST)	NH3 PPB	NH3 STD ERROR PPB	
S011	11/11/87	0000	0550	18.51	0.93	
S012		0600	0950	13.06	0.65	
S013	(315)	1000	1350	12.30	0.61	
S014		1400	1750	7.84	0.39	
S015		1800	2350	13.40	0.67	
S021	11/12/87	0000	0550	14.87	0.74	
S022		0600	0950	5.80	0.29	
S023	(316)	1000	1350	5.68	0.28	
S024		1400	1750	5.21	0.26	
S025		1800	2350	4.64	0.23	
S031	11/13/87	0000	0550	8.53	0.43	
S032		0600	0950	4.30	0.21	
S033	(317)	1000	1350	2.08	0.21	✻
S034		1400	1750	2.18	0.22	✻
S035		1800	2350	3.12	0.16	
S041	12/3/87	0000	0550	2.47	0.12	
S042		0600	0950	8.46	0.42	✻
S043	(337)	1000	1350	2.26	0.23	✻
S044		1400	1750	0.63	0.06	
S045		1800	2350	3.42	0.17	
S051	12/10/87	0000	0550	7.66	0.38	
S052		0600	0950	20.60	1.03	
S053	(344)	1000	1350	8.64	0.43	
S054		1400	1750	6.28	0.31	
S055		1800	2350	9.30	0.47	
S061	12/11/87	0000	0550	3.15	0.16	
S062		0600	0950	8.80	0.44	
S063	(345)	1000	1350	4.10	0.20	
S064		1400	1750	3.74	0.19	
S065		1800	2350	10.00	0.50	

✻Estimated value.

LISTING OF THE NO, NO$_2$ AND NOY RESULTS FOR THE SCAQS DATA BASE

PROGRAM NAME: SCAQS
ORGANIZATION: AIHL(CAPEL)
SITE NAME: LONG BEACH
SAMPLER: CHEMILUMINESCENT NOX ANALYZER (TECO 14 B/E WITH DENUDER)
    DASIBI 1003 OZONE MONITOR

SPECIES
  MEASURED: NO, NO2, NOY (NOY=NOx REMOVED BY CARBONATE-COATED DENUDER)
    OZONE
UNITS: PPB(V) UNCORRECTED TO STP
PRECISION: NOT DETERMINED

DATE (JULIAN DATE)	TIME (PST)*	NO (PPB)	NO2 (PPB)	NOY (PPB)	O3 (PPB)
11/11/87	0100	302.99	22.29	5.23	10.16
	0200	173.17	18.42	5.07	7.84
315	0300	110.30	17.65	2.93	6.67
	0400	81.35	17.93	2.39	6.46
	0500	86.03	16.75	2.13	6.53
	0600	76.14	15.61	1.84	6.31
	0700	102.49	16.82	1.50	4.21
	0800	142.39	22.98	-0.02	7.47
	0900	150.24	47.41	-4.43	8.27
	1000	66.08	47.58	14.04	8.75
	1100	8.43	34.70	5.52	14.98
	1200	<5	39.92	-2.81	23.38
	1300	<5	36.29	3.79	35.93
	1400	<5	25.59	0.36	46.55
	1500	<5	39.64	-14.91	49.77
	1600	<5	86.72	-0.86	31.01
	1700	11.94	69.59	8.27	11.61
	1800	7.75	55.94	1.62	10.53
	1900	16.18	51.61	4.56	10.25
	2000	12.20	49.65	0.03	10.78
	2100	62.17	49.12	2.98	10.33
	2200	255.01	34.04	6.95	11.76
	2300	236.59	33.91	4.26	11.38
	2400	258.06	25.60	8.27	11.85
11/12/87	0100	372.93	26.39	6.08	13.31
	0200	361.48	28.11	4.63	12.71
(316)	0300	345.84	29.07	4.38	12.56
	0400	333.33	26.22	9.66	12.27
	0500	327.86	23.09	7.10	12.17
	0600	337.17	22.20	4.55	12.09
	0700	392.73	24.52	3.87	13.52
	0800	386.00	37.84	-0.31	14.44
	0900	199.86	58.38	-5.33	12.33
	1000	77.24	74.81	5.93	12.56

	1100	19.32	85.23	-5.69	17.59
	1200	15.31	88.71	2.85	21.14
	1300	<5	70.51	-1.59	33.03
	1400	<5	84.17	8.10	53.79
	1500	<5	58.50	3.11	58.86
	1600	<5	53.96	-4.12	43.45
	1700	<5	98.55	-7.76	18.00
	1800	20.84	72.91	12.44	11.40
	1900	27.59	47.14	8.13	8.99
	2000	37.05	39.02	4.20	8.41
	2100	62.90	32.69	4.82	8.64
	2200	122.06	23.38	6.37	9.68
	2300	160.35	21.76	1.38	9.94
	2400	119.10	26.48	4.34	9.62
DATE (JULIAN DATE)	TIME (PST)	NO (PPB)	NO2 (PPB)	NOY (PPB)	O3 (PPB)
11/13/87	0100	155.69	27.97	6.03	10.43
	0200	73.97	33.56	4.48	8.65
(317)	0300	36.14	33.82	4.63	8.10
	0400	55.26	29.77	5.77	8.60
	0500	24.56	34.01	-5.45	8.09
	0600	29.57	26.33	5.96	9.16
	0700	5.76	23.02	4.19	9.85
	0800	11.45	24.79	1.98	11.30
	0900	12.83	31.06	1.30	11.14
	1000	<5	24.01	7.55	16.62
	1100	<5	12.84	1.94	26.72
	1200	<5	16.35	-0.56	27.56
	1300	<5	18.29	0.36	29.58
	1400	<5	13.20	1.34	31.91
	1500	<5	10.44	-1.42	30.89
	1600	<5	8.97	0.50	29.10
	1700	<5	12.51	0.94	24.51
	1800	<5	20.06	0.60	21.90
	1900	<5	23.79	0.43	19.64
	2000	<5	10.93	6.50	24.82
	2100	<5	11.08	-2.03	27.06
	2200	<5	7.72	0.07	25.70
	2300	<5	10.36	1.97	15.21
	2400	<5	5.05	5.30	11.86
11/14/87	0100	<5	<5	--	17.98
	0200	<5	<5	--	18.52
(318)	0300	<5	7.08	-0.35	14.86
	0400	<5	6.95	1.34	12.76
	0500	<5	10.34	0.28	11.07
	0600	11.34	12.08	2.05	10.07
	0700	7.33	13.98	1.45	9.67

DATE (JULIAN DATE)	TIME (PST)	NO (PPB)	NO2 (PPB)	NOY (PPB)	O3 (PPB)
12/3/87	0100	286.38	20.37	4.05	26.05
	0200	297.68	15.58	15.45	24.33
(337)	0300	334.58	17.45	10.39	21.50
	0400	337.45	25.90	8.76	20.64
	0500	345.72	32.57	11.56	21.66
	0600	361.47	24.39	11.86	20.63
	0700	418.74	32.79	13.53	22.53
	0800	518.42	46.06	6.98	24.62
	0900	485.02	83.36	8.09	26.29
	1000	146.58	41.23	17.17	23.82
	1100	88.80	120.98	-64.6**	27.49
	1200	82.17	169.32	13.48	32.16
	1300	20.73	133.74	-2.03	37.82
	1400	19.66	143.31	-0.42	43.85
	1500	10.29	108.80	11.94	58.30
	1600	10.38	99.94	5.51	50.79
	1700	8.82	107.25	15.14	38.91
	1800	11.36	87.75	5.73	26.04
	1900	52.94	73.18	8.31	16.70
	2000	77.89	60.60	13.37	15.80
	2100	96.83	47.61	10.53	15.37
	2200	146.80	38.67	11.38	17.27
	2300	162.29	34.15	11.33	18.84
	2400	206.18	24.67	7.70	18.37
12/10/87	0100	423.83	36.29	9.80	21.33
	0200	411.52	43.93	12.11	20.13
(344)	0300	412.11	42.57	12.23	18.80
	0400	382.44	40.93	8.94	17.01
	0500	395.40	32.39	10.52	15.56
	0600	433.26	32.16	7.85	15.42
	0700	478.36	26.67	10.80	15.15
	0800	430.38	32.56	5.78	15.00
	0900	269.61	56.02	-0.67	13.75
	1000	218.24	90.84	-5.88	14.68
	1100	116.96	126.39	7.76	17.35
	1200	30.26	74.66	11.98	17.70
	1300	18.90	82.58	0.79	24.43
	1400	37.76	156.74	19.57	26.45
	1500	14.13	80.81	24.17	23.77
	1600	14.61	80.78	6.65	21.78
	1700	27.64	58.01	9.05	11.17
	1800	85.85	29.92	9.07	10.20
	1900	156.10	21.40	7.58	12.66
	2000	161.45	22.31	5.69	12.21
	2100	196.49	15.27	5.05	15.60
	2200	248.36	8.72	6.41	14.04
	2300	359.93	<5	9.13	14.50
	2400	330.54	7.72	3.00	15.32

DATE (JULIAN DATE)	TIME (PST)	NO (PPB)	NO2 (PPB)	NOY (PPB)	O3 (PPB)
12/11/87	0100	410.43	31.10	-0.39	18.52
	0200	355.97	27.09	15.25	16.10
(345)	0300	181.77	32.23	3.90	12.62
	0400	195.64	29.73	7.62	13.40
	0500	184.80	27.26	6.00	12.81
	0600	203.96	19.97	3.00	12.48
	0700	266.09	20.21	6.54	12.51
	0800	397.76	24.02	3.01	15.15
	0900	254.27	37.63	5.86	11.26
	1000	87.66	46.82	-0.87	10.22
	1100	58.44	57.12	4.67	15.18
	1200	35.70	59.75	3.52	16.46
	1300	22.79	62.66	0.69	19.86
	1400	22.27	78.05	-1.12	24.76
	1500	17.69	77.26	-5.25	25.33
	1600	49.85	103.61	3.82	22.04
	1700	35.40	95.27	5.54	23.90
	1800	68.99	85.34	7.73	20.48
	1900	107.52	69.60	8.95	22.88
	2000	181.77	49.84	14.41	20.35
	2100	242.68	39.22	12.52	20.05
	2200	311.86	29.36	12.79	19.08
	2300	374.09	31.98	11.48	19.41
	2400	415.15	50.32	9.21	21.42
12/12/87	0100	403.36	53.45	20.53	21.39
	0200	432.31	34.37	24.96	22.73
(346)	0300	481.65	40.20	20.72	23.67
	0400	498.09	39.07	12.27	23.00
	0500	388.28	30.88	14.74	19.19
	0600	342.93	20.06	12.13	16.49
	0700	272.90	14.72	7.17	13.98
	0800	281.67	18.66	5.14	14.67

*Time at end of 1-hr averaging period.
* *Judged inaccurate because of rapidly changing concent